Islamic University Journal of Applied Sciences (IUJAS)
https://journals.iu.edu.sa/jesc

Volume VII, Issue II, December 2025, Pages 137-149

Thermal Properties and Phase Formation in Zn-Modified Pb–Sn Alloys

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Abstract

This study investigates the influence of a 2% zinc (Zn) addition on the thermal properties and crystallization kinetics of a Pb-5Sn solder alloy to understand its impact on processing characteristics. Non-isothermal differential scanning calorimetry (DSC) was employed to analyze the melting and crystallization behavior of both the base Pb-5Sn and the modified Pb-5Sn-2Zn alloys at heating and cooling rates of 5, 10, 15, and 25 °C·min^{-1}. The Kissinger method was applied to the crystallization peak data to determine the activation energy (E_a) for the process. The results revealed a significant decrease in the activation energy for crystallization upon the addition of zinc, from 103.54 kJ/mol for the base Pb-5Sn alloy to 57.93 kJ/mol for the Pb-5Sn-2Zn alloy. Furthermore, the crystallization peak temperatures for the Zn-modified alloy were consistently lower across all cooling rates, indicating an increased propensity for crystallization. This substantial reduction in the energy barrier suggests that zinc atoms act as effective heterogeneous nucleation sites, thereby facilitating the transition from the liquid to the solid phase. These findings demonstrate that minor Zn alloying can significantly alter the phase transformation kinetics, providing a practical route for tailoring the solidification behavior and optimizing the thermal processing for Pb-Sn alloys.

Keywords

DSC; Kissinger; Activation energy; Crystallization; Thermal behavior.

https://doi.org/10.63070/jesc.2025.027
Received 16 September 2025; Revised 06 October 2025; Accepted 11 October 2025.
Available online 12 October 2025.
Published by Islamic University of Madinah on behalf of *Islamic University Journal of Applied Sciences*.

1. Introduction

Lead–tin (Pb–Sn) solder alloys have long been established as essential materials in soldering and electronic packaging due to their favorable characteristics, including low cost, a eutectic melting temperature near 183 °C for the eutectic composition, and excellent wettability on a wide range of metallic substrates [1,2]. Depending on their composition, these alloys exhibit either a sharp eutectic melting point or an extended "pasty" range, offering versatility that has made them indispensable in various high-reliability joining applications, particularly within the aerospace, automotive, and defense industries. In recent years, the drive for materials with tailored thermal and mechanical performance has prompted research into modifying these traditional alloys [3]. An established strategy for enhancing the performance of binary alloys involves the micro-addition of a third alloying element. This approach can refine the microstructure, improve mechanical properties such as tensile strength and creep resistance, and alter the solidification kinetics. Among various potential elements, zinc (Zn) has garnered significant attention. Zinc is an inexpensive element known for its ability to modify the microstructure and mechanical behavior of solders [4, 5]. The Pb–Sn–Zn ternary alloy system represents a distinct subset where the incorporation of zinc is expected to alter both the thermodynamic and kinetic parameters governing phase transformations during solidification. The influence of zinc in solder alloys is multifaceted. Recent research indicates that minor element additions, like zinc, can significantly impact the thermodynamic properties, phase formation processes, and kinetic behavior of solders, providing a path for precise control over alloy performance during manufacturing [6-9]. In lead-free solder systems, such as Sn-Ag-Cu (SAC) alloys, minor zinc additions have been shown to improve wetting characteristics and suppress the formation of brittle intermetallic compounds [10]. In lead-based systems, zinc addition can refine the grain structure and influence the morphology of the eutectic phases, which directly influences the material's durability and strength. These microstructural changes are intrinsically linked to the alloy's thermal behavior [11]. Zinc's incorporation modifies melting and solidification characteristics, potentially shifting transformation temperatures and influencing the energy barrier required for nucleation and growth during crystallization. Despite the importance of this ternary system, systematic investigations into the non-isothermal thermal behavior and crystallization kinetics of Zn-modified Pb–Sn alloys remain relatively limited [12-15] Advanced thermal analysis techniques, particularly Differential Scanning Calorimetry (DSC), provide a precise means of characterizing these alloys. DSC allows for the identification of critical phase transformation temperatures such as onset, peak, and completion of melting and crystallization—while also enabling the determination of key kinetic parameters, like the activation energy (E_a), using established models such as the Kissinger method. Such information is essential for comprehensively describing an alloy's behavior under the dynamic thermal conditions typical of manufacturing processes [16,17].

The present study provides a detailed thermodynamic and kinetic analysis of a binary Pb-5Sn alloy and a ternary Pb-5Sn-2Zn alloy, with a particular focus on quantifying the influence of zinc addition. By examining phase transformation temperatures and calculating the activation energy for crystallization under varying cooling rates, this work seeks to deliver practical insights for tailoring alloy compositions and optimizing processing for modern soldering and manufacturing applications.

2. Experimental Work

2.1. Materials and Alloy Preparation

Two alloys with the nominal compositions Pb-5wt%Sn (referred to as Pb-5Sn) and Pb-5wt%Sn-2wt%Zn (referred to as Pb-5Sn-2Zn) were prepared for this study. High-purity primary metals (99.999%) of lead, tin, and zinc were used. Precisely weighed amounts of the constituent metals were placed in a graphite crucible within a furnace. The melt was maintained at a temperature of 700 °C for 20 minutes with mechanical stirring to ensure complete chemical homogeneity. The melt was then cast into steel molds filled with paraffin oil to prevent air exposure during casting and was left to cool to room temperature. Subsequently, the as-cast alloys were treated at 438 K for 50 hours.

2.2. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) analysis was performed using a Labsys Evo thermal analyzer under a continuous flow of high-purity argon to prevent oxidation during heating. The samples, weighing approximately 40 mg, were placed in alumina crucibles. The melting and crystallization temperatures were recorded from the endothermic and exothermic peaks during the heating and cooling cycles, respectively. Each thermal cycle was repeated three times to ensure experimental reproducibility, and the deviation of the measured peak temperatures was within ±0.8 °C. The applied heating and cooling rates were 5, 10, 15, and 25 °C min^{-1}, ensuring consistency across all measurements. This approach allowed for an accurate evaluation of thermal transitions and minimized uncertainty in determining the onset and peak temperatures. The activation energy (E_a) associated with the crystallization process was estimated based on the Kissinger method.

3. Results and Discussion

3.1. Analysis of the Differential Scanning Calorimetry (DSC) Curves

The DSC thermograms for both the Pb-5Sn and Pb-5Sn-2Zn alloys are presented in Figures 1 and 2, respectively. Figures 1(a) and 2(a) clearly show the presence of two main phase transformations for each alloy. The first transformation is an endothermic peak, directed downwards, which corresponds to the melting process during the heating cycle. The second transformation is an exothermic peak, directed upwards, which is attributed to the crystallization process during the cooling cycle. This behavior is the typical thermal signature of crystalline materials undergoing melting and solidification.

3.2. Influence of Thermal Rate on Melting and Crystallization Kinetics

Figures 1(b) and 2(b) focus on the melting peaks. A systematic shift in the melting peak temperature towards higher values is observed with an increasing heating rate (β). For example, in Figure 1(b), the melting peak at a rate of 25 °C/min occurs at a higher temperature than that at 5 °C/min. This phenomenon is a known kinetic effect attributed to the thermal lag between the heating source (the furnace) and the sample. At higher rates, the system requires more time to reach thermal equilibrium, leading to the peak being recorded at an apparently higher temperature. Conversely, an opposite kinetic effect is observed during the cooling cycle.The upper portions of the curves in Figures 1(a) and 2(a) show a strong dependence of the crystallization process on the cooling rate. The crystallization peak temperature shifts significantly towards lower temperatures as the cooling rate increases. This effect is the essence of kinetic studies. The crystallization process requires a thermodynamic driving force in the form of undercooling to initiate. The higher the cooling rate, the shorter the time available for the formation and growth of crystalline nuclei, and thus the system requires a greater degree of undercooling (i.e., a lower temperature) to stimulate the solidification process, which explains this large shift.

3.3. Effect of Zinc Addition

By comparing Figure 1(b) with Figure 2(b), it can be observed that the addition of 2% zinc leads to a slight decrease in the melting temperature. The melting peak for the Pb-5Sn-2Zn alloy occurs at slightly lower temperatures than that of the Pb-5Sn alloy at the same heating rates. This indicates that zinc alters the phase equilibrium diagram of the Pb-Sn system, shifting the composition towards a region with a lower melting temperature. When comparing the crystallization peaks (in Figures 1(a) and 2(a)), it is found that the addition of zinc significantly alters the solidification kinetics. By comparing Figure 1(b) with Figure 2(b), it can be observed that the addition of 2% zinc leads to a slight decrease in the melting temperature. The melting peak for the Pb-5Sn-2Zn alloy occurs at slightly lower temperatures than that of the Pb-5Sn alloy at the same heating rates. This indicates that zinc alters the phase equilibrium diagram of the Pb-Sn system, shifting the composition towards a region with a lower melting temperature. When comparing the crystallization peaks (in Figures 1(a) and 2(a)), it is found that the addition of zinc significantly alters the solidification kinetics.

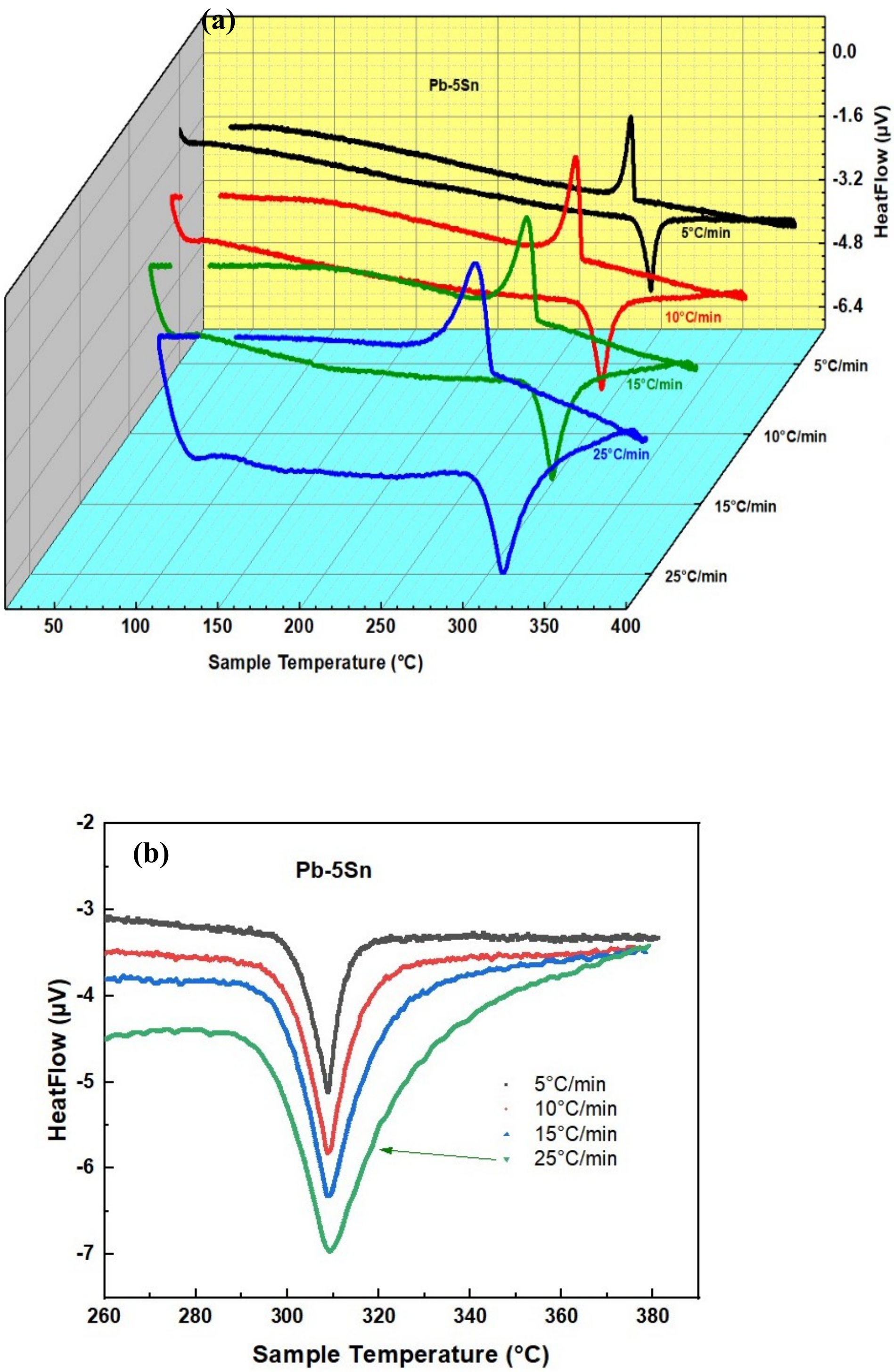

Figure 1. DSC curves for the Pb-5Sn alloy: (a) plot showing full heating and cooling cycles at rates of 5, 10, 15, and 25 °C/min; (b) Detailed view of the endothermic melting peaks at different heating rates.

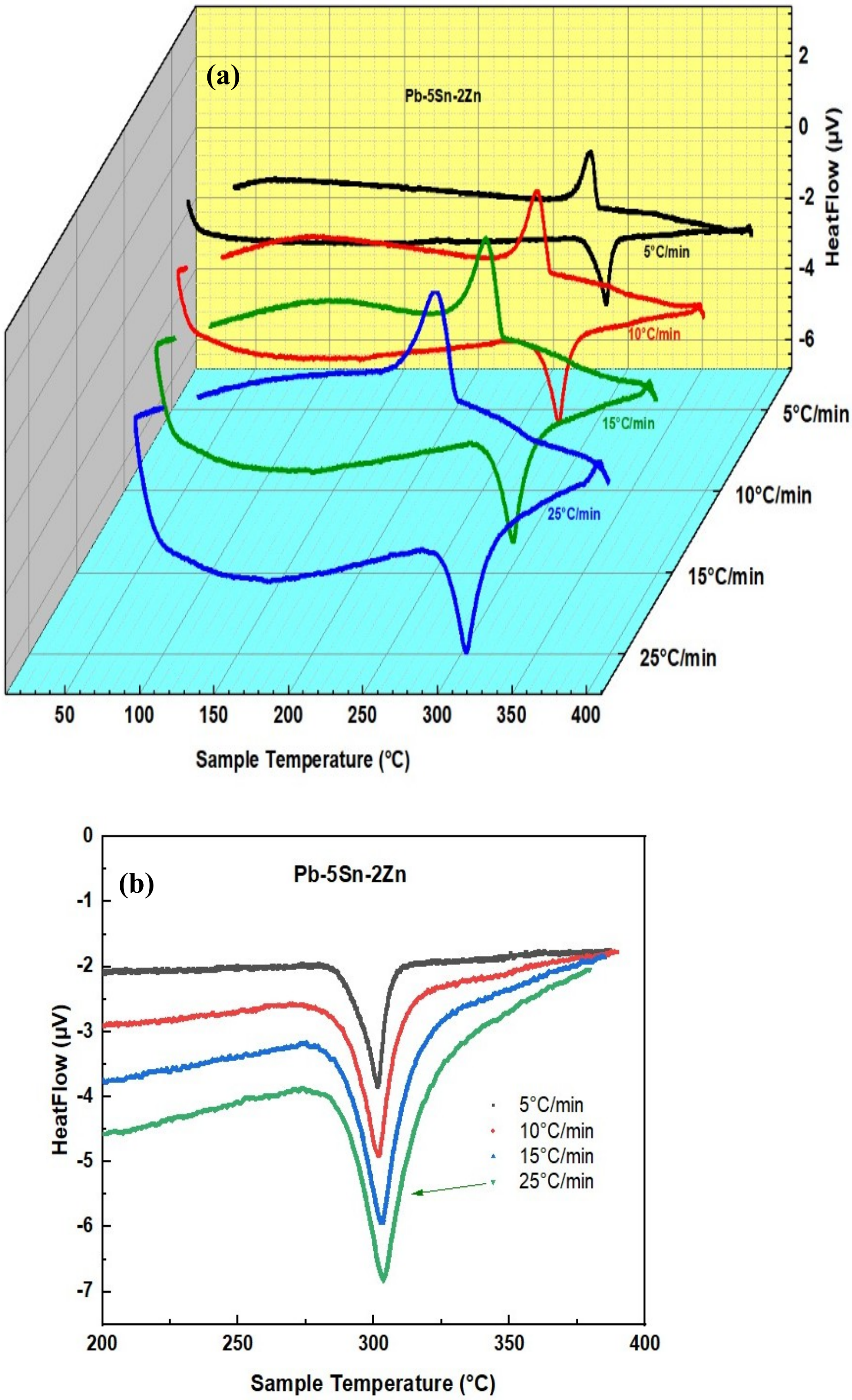

Figure 2. DSC curves for the Pb-5Sn-2Zn alloy: (a) plot showing full heating and cooling cycles at rates of 5, 10, 15, and 25 °C/min; (b) Detailed view of the endothermic melting peaks at different heating rates.

A direct visual comparison of the curves (Figure 3a) shows that the addition of zinc fundamentally alters the thermal response, shifting the melting and crystallization events towards lower temperatures. This conclusion is quantitatively confirmed in Figure 3(b), which illustrates that the melting temperature of the Pb-5Sn-2Zn alloy is consistently about 5-6 °C lower than the base alloy across all heating rates. This decrease in the melting temperature is a thermodynamic effect, reflecting a modification in the phase equilibrium diagram of the Pb-Sn-Zn system, whereas the slight increase in melting temperature with an increasing heating rate in both alloys is an expected result of thermal lag. Regarding the crystallization behavior, a more pronounced kinetic effect is observed, where the crystallization temperature sharply decreases with an increasing cooling rate for both alloys, confirming that the solidification process requires a driving force in the form of undercooling to initiate. The addition of zinc also significantly lowers the crystallization temperatures. This behavior is consistent with findings reported in the literature [18, 19].

3.2. Kissinger Analysis of the Activation Energy for the Crystallization Process

Data was extracted from experimental measurements and organized in the Table 1, which shows the crystallization temperatures at different cooling rates (β). A comprehensive analysis of the experimental data related to the crystallization of two alloys, Pb-5Sn and Pb-5Sn-2Zn, is presented. The objective is to calculate the activation energy (E_a) for the crystallization process of each alloy using the Kissinger method and to analyze the effect of zinc (Zn) addition on this property. The Kissinger method is based on the following linear relationship [20].

$$ln\left(\frac{\beta}{T_p^{\,2}}\right) = -\frac{E_a}{(R \times T_p)} + C \ ,$$

Where T_p represents the absolute crystallization temperature (in Kelvin). The necessary variables for applying linear regression were calculated for each alloy.

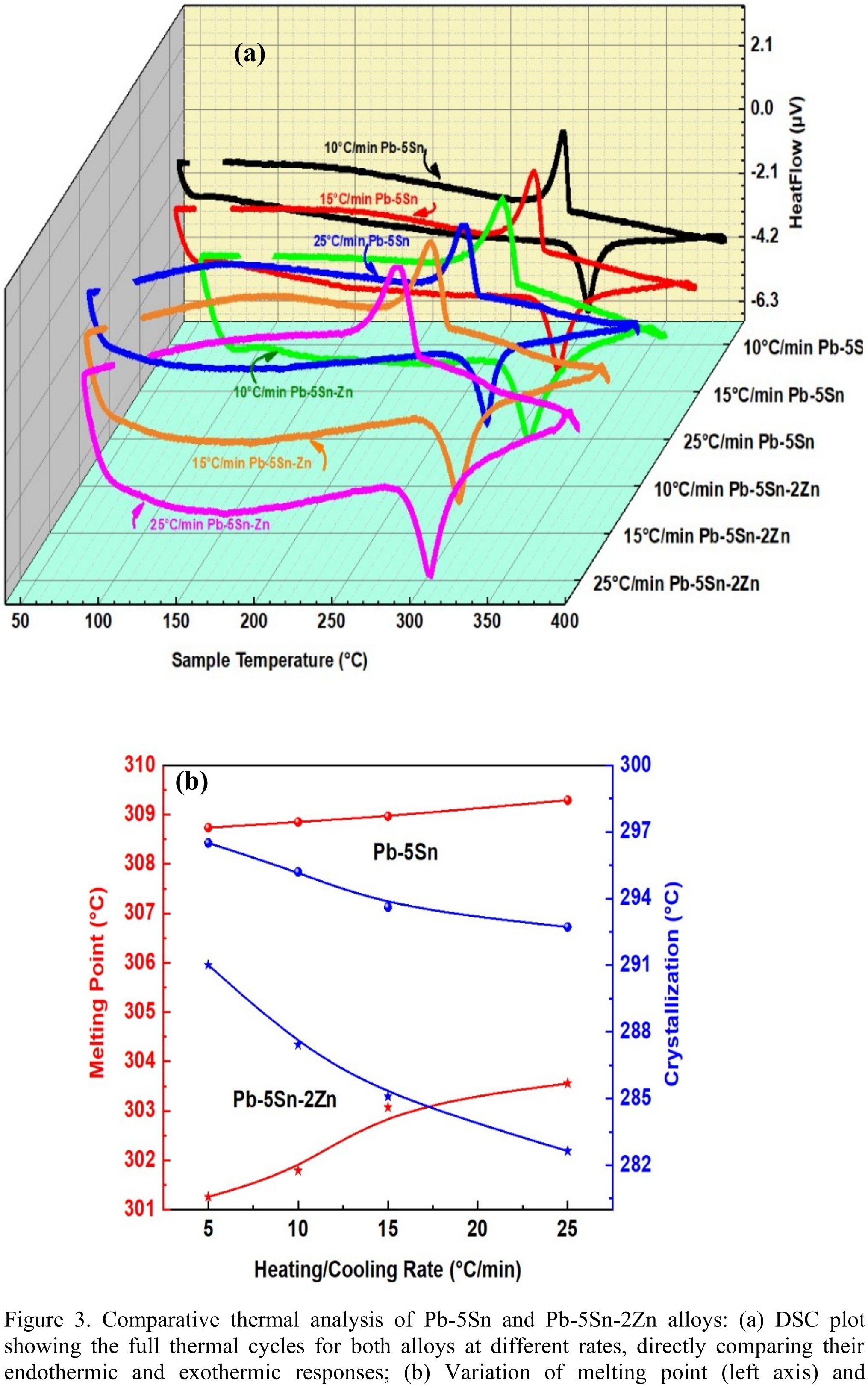

Figure 3. Comparative thermal analysis of Pb-5Sn and Pb-5Sn-2Zn alloys: (a) DSC plot showing the full thermal cycles for both alloys at different rates, directly comparing their endothermic and exothermic responses; (b) Variation of melting point (left axis) and crystallization temperature (right axis) as a function of the heating/cooling rate.

Table 1: Kissinger Method Calculation Data for Determining Activation Energy.

Alloy	β (°C/min)	T_p (K)	$1/T_p$ (K^{-1})	$\ln(\beta/T_p^2)$
Pb-5Sn	5	569.655	0.0017555	-10.992
	10	568.346	0.0017595	-10.380
	15	566.767	0.0017644	-10.002
	25	565.869	0.0017672	-9.516
Pb-5Sn-2Zn	5	564.157	0.0017726	-11.082
	10	560.567	0.0017839	-10.370
	15	558.237	0.0017914	-9.998
	25	555.786	0.0017993	-9.519

The relationship between $\ln(\beta/T_p^2)$ and $1/T_p$ was plotted for each alloy as shown in figure 4. The slope of the resulting straight line (m) is related to the activation energy (E_a) by the equation $E_a = -m \times R$, where R is the universal gas constant (8.314 J/mol·K). The results yielded an activation energy (E_a) of 103.54 kJ/mol for the Pb-5Sn alloy and an activation energy (E_a) of 57.93 kJ/mol for the Pb-5Sn-2Zn alloy. The linear regression results showed excellent data fit, with R^2 values of 0.989 for the Pb-5SnPb-5Sn alloy and 0.999 for the Pb-5Sn-2ZnPb-5Sn-2Zn alloy.

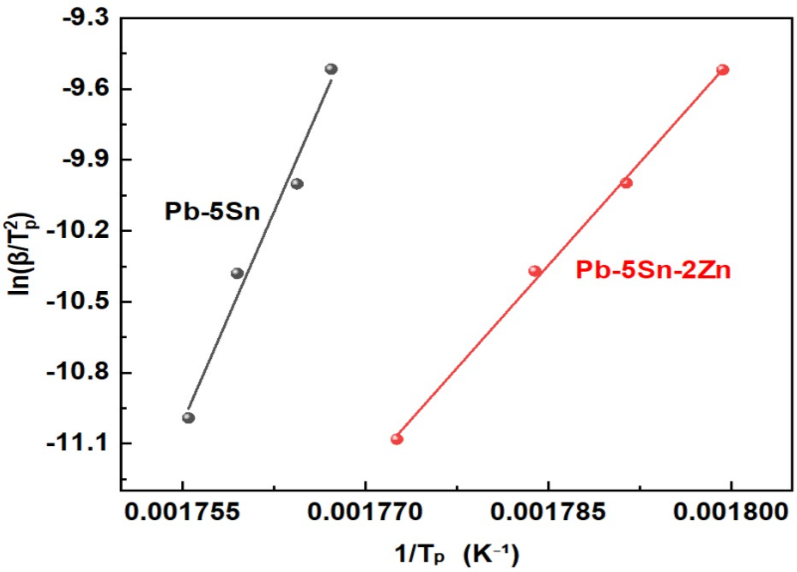

Figure 4. Kissinger plots $\ln(\beta/T_p^2)$vs $1/T_p$ used to estimate the crystallization activation energy for Pb–5Sn and Pb–

The results clearly show that the activation energy for the crystallization process in the Pb-5Sn alloy (103.54 kJ/mol) is significantly higher than that of the Pb-5Sn-2Zn alloy (57.93 kJ/mol). This considerable decrease in activation energy indicates that the addition of 2% zinc (Zn) to the lead-tin alloy significantly facilitates the crystallization process. This can be explained by the possibility that zinc atoms act as effective nucleation sites, which lowers the energy barrier required for the initiation of crystal formation during the alloy's cooling. This means the zinc-containing alloy requires less energy to transition from the liquid (or amorphous) state to the stable crystalline state, making the crystallization process faster and easier. Upon reviewing scientific literature, it is found that the activation energy values for lead-tin alloys vary depending on the precise composition and experimental conditions. For example, these values can be affected by the presence of other elements or by the heating and cooling rates used [21, 22]. In general, adding a third element to a binary alloy can significantly alter the kinetics of the crystallization process. Studies on other alloys, such as magnesium-zinc alloys, have shown that the addition of elements like platinum or silver changes the activation energy and enhances thermal stability [23-24]. Similarly, in other systems, it has been observed that the addition of extra elements can either facilitate or hinder the crystallization process.

4. Conclusion

In this study, the influence of adding 2 wt.% zinc (Zn) on the thermal properties and crystallization kinetics of a Pb-5Sn solder alloy was successfully investigated using Differential Scanning Calorimetry (DSC) at various cooling and heating rates. The following key conclusions have been drawn:

1. The addition of zinc demonstrated a twofold effect on the alloy's thermal properties; it led to a significant decrease in both the melting temperature (by approx. 5–6 °C) and the crystallization temperature across all tested rates. This indicates that zinc not only alters the thermodynamic equilibrium of the system but also significantly influences the kinetics of the solidification process.
2. The analysis of crystallization kinetics using the Kissinger method proved that zinc addition drastically lowers the apparent activation energy for crystallization (E_a). The value decreased from 103.54 kJ/mol for the base Pb-5Sn alloy to 57.93 kJ/mol for the modified Pb-5Sn-2Zn alloy, a reduction of approximately 44%.
3. This substantial reduction in the energy barrier is attributed to the role of zinc atoms acting as effective heterogeneous nucleation sites within the melt. These sites facilitate the onset of solidification by providing favorable low-energy surfaces for the formation of crystalline nuclei, thereby significantly lowering the energy required to activate the crystallization process.

4. The results confirm that minor zinc additions effectively modify the solidification of Pb-Sn alloys by facilitating nucleation, which is key to refining the microstructure and enhancing mechanical properties. These insights can be used to optimize thermal processing in industrial applications, such as reflow soldering. Future work should investigate different zinc concentrations and perform mechanical analysis to fully correlate kinetic changes with structural performance.

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