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INTERMETALLIC COMPOUNDS FORMATION IN TRANSIENT LIQUID PHASE Sn–Ag–Ni ALLOYS VIA MULTIPLE REFLOW CYCLES

This study qualitatively demonstrates the role of Ni addition on transient liquid phase (TLP) Sn–Ag–Ni solder alloy through multiple reflow cycles, focusing on the formation, stability, and transformation of intermetallic compounds (IMCs). The optimal incorporation of 0.3 wt.% nickel (Ni) into the Sn–Ag solder alloy promotes the formation of thermally stable, high-melting-point IMCs, enhancing the structural integrity of the solder joint. Phase diagram analysis using Thermo-Calc software qualitatively confirms the coexistence of Ag_3Sn, Ag_4Sn, and Ni_3Sn_4 with the β-Sn phase, supporting their structural role in solder joint stability. Thermodynamic analysis shows that Ag_3Sn IMC has the highest favorability for formation and stability at room temperature, while Ni_3Sn_4 IMC enhances high-temperature performance. Differential Scanning Calorimetry (DSC) analysis qualitatively supports these findings, revealing two distinct melting peaks. The first peak relates to the eutectic melting temperature, while the second peak relates to the high melting temperature. The Sn–Ag–Ni solder alloy is more thermally stable than Sn–Ag. Heat flow data indicate enhanced phase transformations and improved thermal stability in Ni-containing solder alloy. This study provides a qualitative understanding of the addition of Ni and its effects on the IMC evolution, phase inter-reaction, and high-temperature reliability critical for optimizing lead-free solder alloys in electronic packaging applications.

Keywords: Transient liquid phase; Multiple reflow cycles; Nickel addition; High-temperature solder

1. Introduction

The rapid development of electronic devices has highlighted the critical need for advanced soldering materials that can withstand increasingly demanding operating conditions while maintaining superior reliability to ensure the integrity of electronic packaging. The synthesis of transient liquid phase (TLP) solder alloys through multiple reflow cycles represents a promising approach to promote the formation of high-temperature intermetallic compounds (IMCs) at a lower bonding temperature. The mechanism of TLP soldering involves multiple reflow cycles during which the solder alloy undergoes phase transformation, leading to the formation of both low and high melting points IMCs. This process is pivotal in creating solder joints that exhibit superior thermal stability [1-3].

The electronic packaging industry has traditionally relied on high-Pb solder alloys for high-power module applications due to the excellent wettability, and good mechanical properties. However, extensive research and development efforts are currently directed toward lead-free alternatives due to health and environmental concerns [4,5]. The traditional lead-free solder alloys, Sn–Ag solder alloys, have demonstrated reasonable performance as well as health and environmental benefits in conventional applications. However, as modern devices push the boundaries of thermal limits, the limitations of these binary alloys become increasingly apparent [6,7].

The incorporation of alloying elements, for instance, antimony (Sb), indium (In), gallium (Ga), phosphorus (P), improves the thermal and mechanical behavior due to its effect to the microstructural evolution and IMC formation, and subsequently to the bonding reliability and properties in elevated-temperature electronic packaging applications [4,8,9]. The introduction of Ni as an alloying element in Sn–Ag solder alloy opens up novel possibilities for enhancing the solder joint reliability, including acts as a facilitator of uniform IMC formation and an inhibitor of detrimental IMC formation, thereby aiding in achieving robust

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and reliable solder joints, particularly through multiple reflow cycles. The innovative soldering technique and the addition of Ni lies in its unique ability to form more thermally stable IMCs.

The interaction between different elements during multiple reflow cycles presents an intriguing scientific challenge, as these elements must work synergistically to form a stable, high-performance solder joint. The formation and stability of IMCs remain the subject of intensive investigations, especially their role in enhancing solder joint reliability under harsh operating conditions. A comprehensive investigation combining advanced theoretical modeling with rigorous experimental analysis was conducted to investigate the synthesis process of Sn–Ag–Ni solder alloys through multiple reflow cycles.

The phase diagram analysis using computational tool provides valuable insights into the coexistence of multiple phases, which contribute to the enhanced thermal stability. Thermo-Calc software plays a key role in validating the formation of transient liquid phase solder alloys by analyzing phase transformations and thermodynamic behavior using calculated phase diagrams. The with Differential scanning calorimetry (DSC) analysis offers detailed insight into the melting behavior, thermal stability, and potential suitability for high-reliability applications in the electronic packaging industry.

In short, this study aims to elucidate the formation mechanism, phase transformations, phase stability, thermodynamic properties, and thermal stability of IMCs in Sn–Ag–Ni solder alloys through multiple reflow cycles, combining Thermo-Calc software for theoretical phase diagram analysis with DSC for experimental thermal characterization.

2. Experiment

2.1. Materials and sample preparation

The materials used, including 99.9% pure granular tin (Sn), 99.9% pure granular silver (Ag) and 99.9% pure granular nickel (Ni). After the melting process, each material was cast into a mold and pure Sn, Ag and Ni were then rolled into foil form. The foil samples were rinsed in an ultrasonic bath using acetone for 5 minutes to remove the possible contamination on the samples before sandwiching the structure. After the cleaning process, and then the foil samples were cut into small pieces with approximately 5 mm × 5 mm (length × width). The foil samples were subsequently sandwiched into the Ag/Ni/Sn/Ni/Ag structure, and the weight of each sandwiched sample was 1 g. The Ag/Ni/Sn/Ni/Ag sandwich structure was then placed into the reflow oven for the reflow soldering process with the temperature of 285°C. The sandwiched Ag/Ni/Sn/Ni/Ag undergoes multiple reflow cycles, up to six cycles, in the reflow oven. The reflow profile is shown in Fig. 1.

2.2. Testing and characterization

The phase diagrams and thermodynamic calculations of the solder alloys were performed using Thermo-Calc software 2021a with the TCSLD 3.3 thermodynamic database to calculate phase stability and thermodynamic properties. Furthermore, the Gibbs free energy of different phases in the solder system was calculated using Thermo-Calc software to understand the phase stability and transformation under high temperature conditions. Additionally, DSC was used to determine the melting temperature and heat flow of the solder alloy. Thermal analysis was done using a Mettler Toledo DSC 822 (Mettler Toledo, Greifensee, Switzerland) provided by Universiti Putra Malaysia (UPM).

3. Results and discussion

3.1. Phase diagram analysis

A phase diagram is a graphical representation that shows the phases present in a material system at equilibrium as a function

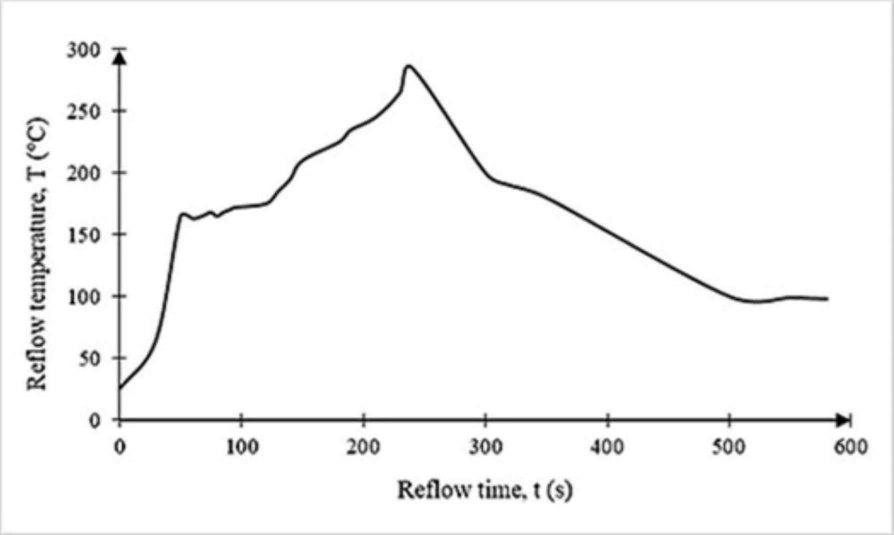
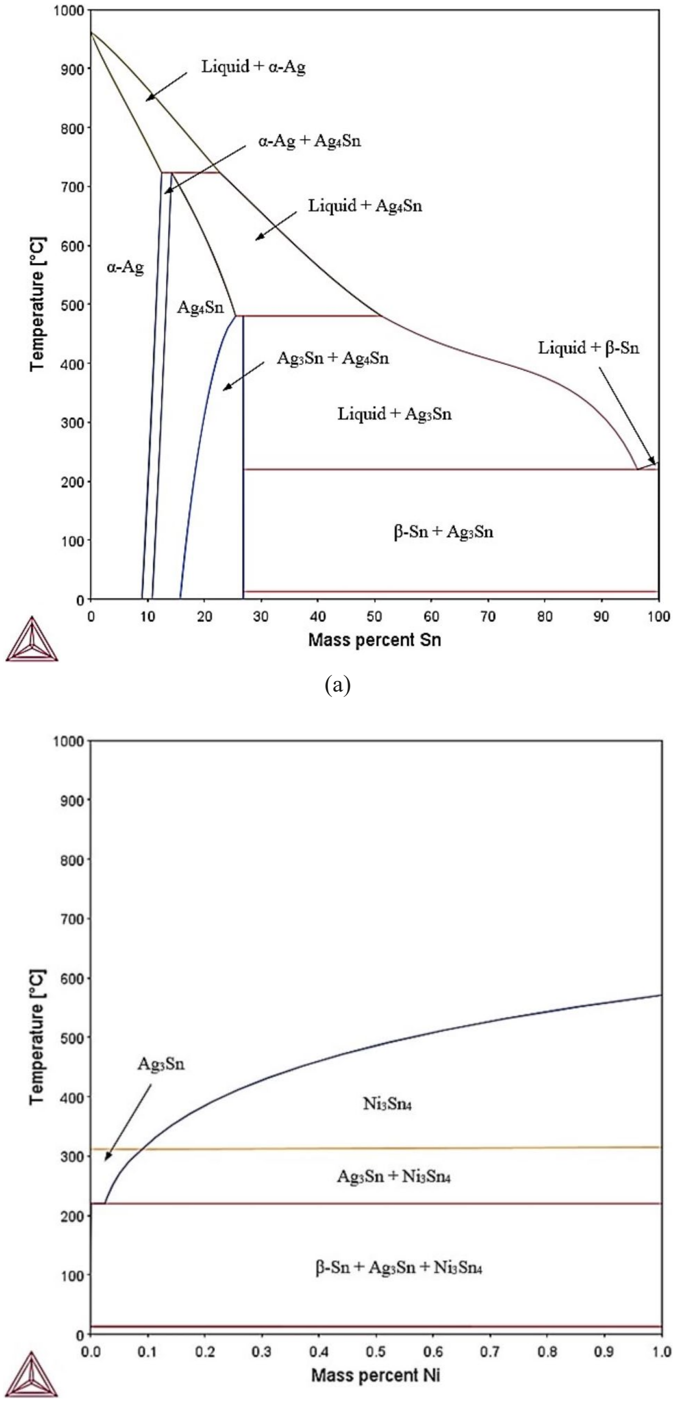


Fig. 1. The reflow profile

of composition and temperature. Fig. 2(a) shows the calculated Sn–Ag phase diagram and Fig. 2(b) shows the calculated Sn–Ag–Ni phase diagram.



(a)

(b)

Fig. 2. The calculated (a) Sn–Ag phase diagram and (b) Sn–Ag–Ni phase diagram

The eutectic reaction involves the simultaneous growth of the β-Sn phase and the IMC Ag_3Sn phase, forming a matrix of β-Sn with Ag_3Sn IMC phase particles distributed within it. When Ni is added to the Sn–Ag solder alloy, multiple phases begin to arise at the interface of the Sn–Ag–Ni solder alloy. As calculated in Fig. 2, at a temperature of about 250°C, the Ag_3Sn phase and Ni_3Sn_4 phase coexist with the β-Sn phase in the Sn–Ag–Ni solder alloy. The coexistence of multiple phases indicates the formation of eutectic IMCs, in which the phases co-nucleate and grow cooperatively in the β-Sn matrix. Increasing the temperature results in the sequential formation of phases, transitioning from solely β-Sn phase + Ag_3Sn phase + Ni_3Sn_4 phase to Ag_3Sn phase + Ni_3Sn_4 phase to Ni_3Sn_4 phase.

According to the concepts of thermodynamic, the Gibbs energy of formation and enthalpy of formation provides insights into the formation and stability of IMCs. Regarding the Gibbs energy of formation, the IMCs with greater released energy are easier to initially form, and a negative value indicates that IMCs is thermodynamically stable [10]. The Gibbs energy of formation for Ag_3Sn IMC and Ag_4Sn IMC at 298 K are −18.6521 kJ/mol and −16.2351 kJ/mol respectively. In addition, a negative enthalpy of formation reveals that the exothermic reaction releasing energy during the formation of the IMC contributes favourably to the stability. A lower value generally represents a more stable IMC, as a higher value develops a higher energy IMC, which tends to be more reactive and less stable [10,11]. The enthalpy of formation for Ag_3Sn IMC and Ag_4Sn IMC at 298 K are −3.3329 kJ/mol and −2.5051 kJ/mol respectively. Based on the calculated Gibbs energy of formation and enthalpy of formation, the Ag_3Sn IMC is more likely to form first and is more stable than the Ag_4Sn IMC at 298 K.

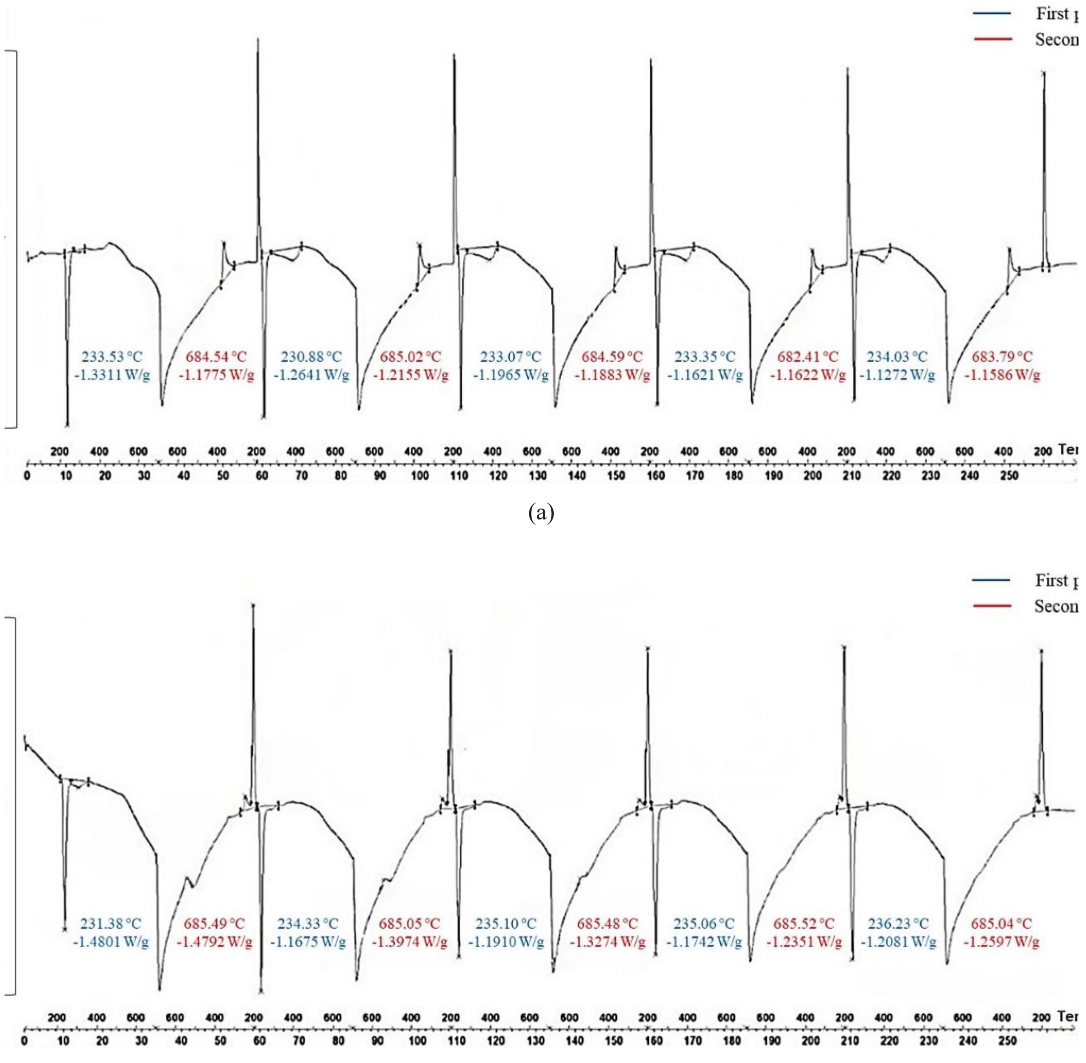
Besides that, the Gibbs energy of formation and the enthalpy of formation are thermodynamic parameters used to evaluate the feasibility and stability of IMC formation. A smaller Gibbs energy of formation and enthalpy of formation means that the IMC is easier to form and more energetically stable. The combination of a negative Gibbs energy of formation and a positive enthalpy of formation indicates that the formation of the IMC is thermodynamically favourable, but it is associated with an endothermic process, meaning that the stability is achieved by absorbing heat during the formation process [12,13]. At 723 K, the Ag_3Sn IMC, Ag_4Sn IMC and Ni_3Sn_4 IMC have respective Gibbs energy of formation of −45.2652 kJ/mol, −39.9246 kJ/mol and −44.4555 kJ/mol, and enthalpy of formation of 16.5555 kJ/mol, 7.9268 kJ/mol and 18.5176 kJ/mol. According to the calculated Gibbs energy of formation and enthalpy of formation, at elevated temperature, the Ag_3Sn IMC exhibits the highest formation favourability and thermodynamic stability, followed by the Ni_3Sn_4 IMC and finally the Ag_4Sn IMC. Nickel is responsible for the formation of Ni_3Sn_4, an IMC that improves re-melting resistance (250°C). This causes the solder joint to become stable at heats and the different phases during multiple reflows become stable. The study findings show that the addition of Ni is critical in enhancing the high-temperature performance of Sn–Ag solder alloys.

3.2. Thermal analysis

The melting temperature is a key solder property that determines the minimum bonding temperature and maximum operating temperature. In melting temperature analysis, multiple reflow soldering on transient liquid phase Sn–Ag and Sn–Ag–Ni solder alloys is investigated by studying the melting temperature peaks over multiple thermal cycles. The heat flow analysis provides insight into the thermal behavior and thermal stability of solder alloys, which is important for ensuring the reliability and performance of electronic devices. Fig. 3 shows the DSC curves of (a) Sn–Ag and (b) Sn–Ag–Ni solder alloys, with the first peak and second peak in each of the five thermal cycles.

For the first peak melting temperature, the Sn–Ag–Ni solder alloy exhibits a broader range and higher variation but shows a distinct increasing trend, with the average melting temperature slightly higher than Sn–Ag solder alloy. This variation and increase can be attributed to the presence of Ni in the solder alloy. The Ni interacts with the Sn–Ag matrix to form IMCs, and the formation of IMCs undergoes homogenization. This phenomenon accounts for the increasing trend observed in the data. The second peak temperature of the Sn–Ag–Ni solder alloy exhibits greater consistency compared to Sn–Ag solder alloy. This high degree of consistency is critical to the ability of the Sn–Ag–Ni solder alloy to maintain its structural integrity at high temperature, making it appropriate for applications demanding high temperatures. In short, the addition of Ni to the Sn–Ag solder alloy results in a more stable first peak melting temperature, indicating improved thermal stability and reliability of the solder joint, and a consistent second peak melting temperature, emphasizing the robustness of the solder at high temperatures [14,15].

Regarding the first peak heat flow analysis, the Sn–Ag–Ni solder alloy shows a slightly more negative value compared to the Sn–Ag solder alloy, indicating increased energy absorption during the initial melting and phase transition process. The subtle increase in negativity could be attributed to the presence of Ni, which affects the initial phase transition involving the microstructure of the solder alloy and the formation of IMCs, leading to a higher energy requirement for the initial melting and phase transition process [6,16]. Furthermore, the slightly increased endothermic nature in the Sn–Ag–Ni solder alloy implies that the required energy is higher because the contribution of the Ni-based IMCs strengthens the eutectic structure by improving the bonding strength, necessitating higher heat flow to overcome the bond strength within the eutectic region [17].



(a)

(b)

Fig. 3. DSC curves of (a) Sn–Ag and (b) Sn–Ag–Ni solder alloys, with the first peak and second peak in each of the five thermal cycles

A more significant difference is observed in the second peak heat flow, where the Sn–Ag–Ni solder alloy exhibits a more negative heat flow compared to the Sn–Ag solder alloy. The substantial increase in the endothermic reaction reveals that the addition of Ni leads to the formation of high-melting-point IMCs, which require more energy to transform or melt at higher temperatures. In addition, the higher energy absorption required to complete the melting and phase transition process in the Sn–Ag–Ni solder alloy demonstrates the presence of more thermally stable IMCs. These IMCs contribute to improved thermal stability of the solder joints, making it suitable for high-temperature applications where prolonged exposure to elevated temperatures is required [18,19]. Moreover, the refinement of IMCs can occur due to the addition of Ni in Sn–Ag–Ni solder alloy. The formation of fine and uniform IMCs increases the overall interfacial area of the intermetallic phase. This increased interfacial area leads to a higher interfacial energy, which requires more energy to be absorbed during the formation of the IMCs [20-22].

4. Conclusion

This study highlights the successful synthesis and characterization of TLP Sn–Ag–Ni solder alloyshave provided significant insights into the formation and stability of high-temperature IMCs. The detailed phase diagram analysis revealed the coexistence of Ag_3Sn, Ag_4Sn, Ni_3Sn_4, and β-Sn phase in the Sn–Ag–Ni solder alloy. The thermodynamic analysis revealed crucial information about phase stability, with Ag_3Sn IMC showing superior stability at room temperature compared to Ag_4Sn IMC, while Ni_3Sn_4 IMC contributes significantly to high-temperature stability. DSC analysis further validated these findings, showing distinct melting peaks corresponding to eutectic and high-temperature transformations, with the Sn–Ag–Ni solder alloy exhibiting higher thermal stability than the Sn–Ag alloy.

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