KeAi
CHINESE ROOTS GLOBAL IMPACT

International Journal of Innovation Studies

EFFECT OF CU ON RESISTIVITY, MICROSTRUCTURE, AND THERMAL PROPERTIES OF SN-3.5AG LEAD-FREE SOLDER ALLOYS

Samia E. Attia Negm [a,b*], **A.A. Bahgat**[a]

[a] *Department of Physics, Faculty of Science, Al-Azhar University, Nasr City, 11884, Cairo, Egypt*

[b] *Department of General Science – Physics Division, Ibn Sina National College for Medical Studies, P.O. Box No. 31906, Jeddah, 21418, Saudi Arabia*

Abstract

Pb solder may be replaced by Sn-Ag-based solder due to its superior mechanical qualities. Using a melt-spinning process for intermediate-step soldering, the Sn-Ag rapidly solidified from the melt in the current investigation to examine the microstructure, thermal, and electrical characteristics of Sn-3.5Ag, Sn-3.5Ag-0.5Cu, and Sn-3.5Ag-0.7Cu. The four-point probe method was used to test the electrical resistivity of Sn–Ag solder alloys at room temperature and between 340K and 600K. Thermal characteristics were examined using Differential Thermal Analysis. When the hardness of as-cast eutectic samples of Sn-3Ag-0.5Cu and Sn-3.5Ag-0.7Cu Lead-Free solder alloys was examined, the Sn-3.5Ag-0.7Cu had the lowest melting point (215°C), while the Sn-3.5 weight percent Ag solder alloy had the highest (221°C). The attributes of the commercially available Sn-3.5 weight percent Ag eutectic solder alloy were compared with the outcomes of the different solder alloys. Additionally shown and addressed are micro-structure investigations.

Keywords: Lead-free solder alloys; SEM micrographs; DTA, Hardness; Electrical resistivity

1. Introduction

In the electronics industry, soldering is a crucial process that creates mechanical and electrical bonds between electronic components in their packaging. Therefore, soldier performance is crucial to the entire operation of the packaging for the assemblies [1,2]. When considering alternatives to tin-lead solders in electronic soldering, a few key factors are considered. These include the solder's lower melting point, sufficient strength, toxicity-related environmental concerns, good electrical and thermal conductivity, affordability, good wetting qualities, and sufficient availability of the base metal. These characteristics are mostly influenced by the alloy preparation techniques, such as unidirectional solidification, conventional casting, or fast solidification. Furthermore, the working process of the alloys, isochronal, isothermal heat treatments, and aging time all these parameters are mostly affected by the properties of these alloys [3-5]. The development and use of contemporary electronics is highly significant. Every device we use daily is attributed to the electronic universe. The process of soldering is crucial to the assembly of electronic circuits and hardware. It uses alternatives to tin-lead solders, such as solder with a lower melting temperature, sufficient strength, low cost, good electrical and thermal conductivity, adequate strength, and availability in sufficient quantities as far as the base metal is concerned. These characteristics are mostly influenced by the alloy preparation techniques, such as unidirectional solidification, conventional casting, or fast solidification.

The qualities of these alloys also have a major impact on the alloys' working process, isochronal and isothermal heat treatments, and aging time [6,7]. An essential method for assembling electronic devices is soldering. The selection of solder materials is crucial for creating a sound solder bond. The quality of a solder junction is influenced by a number of factors, including solderability, melting point, strength, Young's modulus, thermal expansion coefficient, thermal fatigue, creep characteristics, and creep resistance. In the electronic industry, Sn alloys are probably going to be very promising as an alternative solder. This is due to the fact that lead, an ingredient in most solders, is known to be harmful to human health and to have major negative effects on the environment [8,9]. A solid understanding of surface characteristics including surface tension and interfacial adhesion is required to create a solder devoid of lead. This is because the wettability and creation of suitable solder connections are known to be significantly influenced by these characteristics.

It is anticipated that the solder alloys will exhibit exceptional mechanical and electrical performance together with high levels of dependability [5]. The performance of these alloys was enhanced by the inclusion of additional alloying elements because the binary Pb-free solders' characteristics did not fully satisfy the requirements for usage in electronic packaging. In order to improve the solder alloys' electrical properties, alter their melting point, and stop whisker development, small amounts of copper are frequently added. The following traits and qualities are important when looking for alternatives to tin-lead soldering in electronic soldering: a lower melting point of the solder, sufficient strength, toxicity-related environmental concerns, good electrical and thermal conductivity, affordability, good wetting qualities, and sufficient availability of the base metal. These characteristics are mostly influenced by the alloy preparation techniques, such as unidirectional solidification, conventional casting, or fast solidification. The qualities of these alloys also have a major impact on the alloys' working process, isochronal and iso-thermal heat treatments, and aging time [10–12]. In soldering systems, electrical resistivity, which is inversely related to electric conductivity, is one of the crucial criteria that must be assessed in addition to mechanical and microstructural characteristics. It is often recognized that even in solder joints used to link electronic equipment, a lower electrical resistivity showed a greater flow of electric conductivity. In order to gauge the degree of dependability in terms of functionality and the flow current to electrical devices, attention is given to the solder joint in electrical connections [13–16].

2. Materials and Methods:

2.1. Preparation of the alloy

The samples were synthesized using Sn, Ag, and Cu that were more than 99.99% pure. In order to stop the sample from oxidizing in air, the synthesis for the alloys created in this study was done by melting the ingredients in a Pyrex tube while using a fluxing agent (Colophony). To guarantee homogenization of the melt, the tube was shaken during the more than 15 minutes that the melting was conducted on a benzene flame. The alloy was obtained by breaking the tube after it solidified. By immersing the ingot in pure carbon tetrachloride (CCl_4) for an adequate amount of time, excess flux was eliminated. Using CCl_4 as the immersion solvent, the displacement method was used to determine the sample's density. The results demonstrated that the current preparation process is sufficient for these alloys, as indicated in Table (1).

3. Results and Discussions

3.1 Phase equilibria and alloy design

Each solder system's phase diagram was computed to identify the ideal solder composition. Figure (1) shows that when the Cu content rises to 0.7%, the liquidus temperature falls below 221 °C; however, when the Cu content rises above 0.9%, the liquidus temperature rapidly rises. The liquidus temperature of the Sn–3.5Ag–(0–1.0)Cu system is 219 ± 2 °C. According to Park et al. [17], the reflow process may employ a solder alloy whose liquidus temperature is higher than the reflow temperature. Thus, the three compositions of Sn–3.5Ag, Sn–3.5Ag–0.5Cu, and Sn– 3.5Ag–0.7Cu were selected in this study. Three solder systems Sn–3.5Ag, Sn–3.5Ag–0.5Cu, and Sn–3.5Ag–0.7 Cu were chosen as potential Pb-free solder options based on phase diagram calculations.

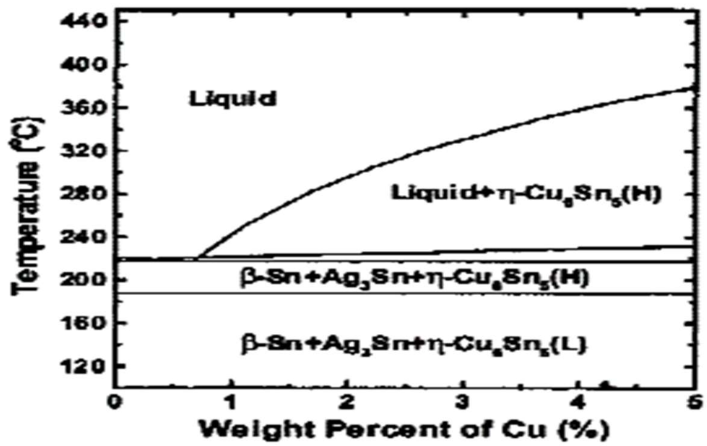


Fig. 1: Calculated phase diagram of Sn-3.5Ag-Cu.

Table 1: Calculated and experimental densities of the pewter Sn solder alloys.

Sample	Alloys	Density calculated	Density Experimental
Sample1	96.5Sn-3.5wt.%Ag	7.04	7.11
Sample2	Sn-3.5Ag-0.5Cu	7.46	7.39
Sample3	Sn-3.5Ag-0.7Cu	7.10	7.01

3.2 Thermal properties of Cu-containing Sn–3.5 Ag solders

Information about the melting or solidification characteristics of alloys is obtained from the results of measurements made using Differential Thermal Analysis (DTA). For instance, the data gathered during overheating or undercooling behaviors is used to extract liquidus and solidus temperatures. The DTA thermograms clearly show two distinctive phenomena. The melting temperature Tm, which is represented by the intersection of the two linear sections that border the DTA's transition shoulder in the endothermic direction, is the first. The second has to do with the endothermic (melting transition) zone. Figures 2a, b, and c, respectively, display the differential thermal analysis thermograms for the eutectic alloys Sn-3.5%Ag, Sn-3.5%Ag-

0.5wt.%Cu, and Sn-3.5%Ag-0.7wt.%Cu. The Sn-3.5, Sn-3.5Ag-0.5Cu, and Sn-3.5 Ag-0.7 Cu alloys' melting points are displayed in Table based on the figures (2).

Table 2: Melting point and heat of fusion of the Sn-Ag solder alloys.

Solder Alloys	M.P (K)	ΔH (cal./gm)
96.5Sn-3.5wt.%Ag	494	8.54
Sn-3.5Ag-0.5Cu	490	6.32
Sn-3.5Ag-0.7Cu	488	6.01

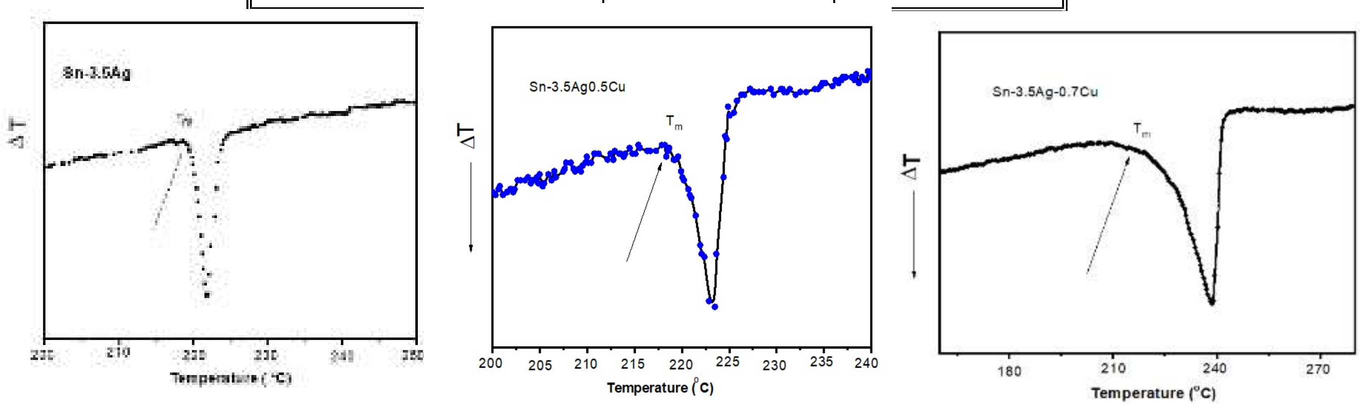


Fig. 2: The differential thermal analysis thermogram of the prepared alloys.

3.2.1 Calculation of Enthalpy (Latent Heat of Fusion)

Enthalpy effects, which happen when solute components are added to a common solvent, are of tremendous interest. By computing the enthalpy generated during the transformation process [18], or the latent heat of fusion, the thermal stability has been examined. By measuring the area under the DTA peak and utilizing Tin as a reference in the DTA calibration curve, the experimental measurement of the enthalpy (ΔH) during the melting process has been established (ΔH_{ref}). Using the formula:

$$\Delta H = \Delta H_{ref}\, A/M \qquad (1)$$

where A is the area under the DTA peak and M is the mass of the sample. The calculated results of enthalpy ΔH are shown in table (2) for Sn-3.5wt.%Ag, Sn-3.5wt.%Ag-0.5wt.% Cu and Sn-3.5wt.%Ag-0.7wt.% Cu alloys respectively.

3.3 The Electrical Resistivity Measurements

Using the four-probe approach, the alloys' temperature dependency d.c. electrical resistivity measurements have been examined. Specimens of any shape can have their resistivity measured using the four-probe approach without the contact resistance interfering. A sensitive thermocouple, a measuring cell with a four-probe electrode, and a specially made oven were used for the measurements. Shielded wires were used to measure the voltage drop and the current. The electric current was supplied by a constant current, D.C. power supply, Model PS-1830 D, and the voltage drop was tracked as a function of temperature using a D.C. micro-voltmeter, Model (HP) 425. Fig. (3) shows the measuring circuit that was employed. By testing a comparatively tiny section of the specimen, the four-probe approach allows one to ascertain the average resistivity value. Therefore, compared to the two-probe method, this approach makes it possible to examine the specimen's homogeneity more effectively.

In measuring the resistivity of large specimens in which the distances between their boundaries and the probes are greater than those between the probes (semi-infinite specimens), the following formula can be used [3-9].

$$\rho = \frac{V_X}{I_X} \frac{2\Pi}{\left(\frac{1}{b_1}\frac{1}{b_3} - \frac{1}{b_1 + b_2}\right) - \left(\frac{1}{b_2 + b_3}\right)} \tag{2}$$

Where, ρ is the resistivity, in ohm. Cm, V_x is the voltage drop between inner probes 2,3, in Volt; I_x is the current following through outer probes 1,4, in Amp. and b_1, b_2, b_3 are the spacing between the probes, in cm. When the spacing between probes is equal, i.e., $b_1 = b_2 = b_3$ the formula is typically, b = 0.5 cm. $\rho = \frac{V_X}{I_X} 2\pi b.$ (3)

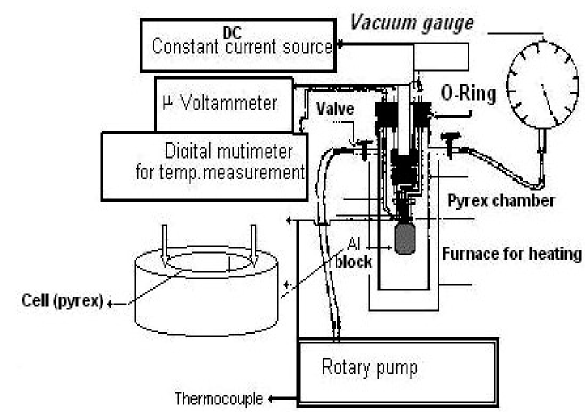


Fig. 3: setup of electrical conductivity.

A metal or alloy's electrical resistivity is mostly determined by its impurities and lattice flaws. Electrical resistivity measurements are typically used to track the precipitation and dissolution processes that occur when alloys are heated [18–21]. The thermo-electrical characteristics of Sn-Ag alloys for various compositions were examined by Ari et al. They discovered that the temperature coefficient of electrical resistivity was unaffected by the Sn, Ag, and Cu compositions and that the resistivity of the samples rose linearly with temperature [22]. Figure (4) displays the isothermal electrical resistivity curves for the Sn-3.5%Ag, Sn-3.5%Ag-0.5Cu, and Sn-3.5%Ag-0.7Cu alloys. Anything that enhances the resistivity, increases the frequency of electron-ion collisions, The conductivity is reduced by plastic deformation of the lattice, foreign atoms in solid solution, and thermal vibration. Therefore, as shown in figures (4), this study finds that the electrical resistivity of the melt-spun alloys under study increases as the temperature rises. The impact of thermal vibration is enhanced by their actions. The rise in electrical resistivity at higher temperatures can be seen as the result of electron-phonon collisions, and the thermal disturbance of the lattice can be explained in terms of quantified elastic waves or phonons.

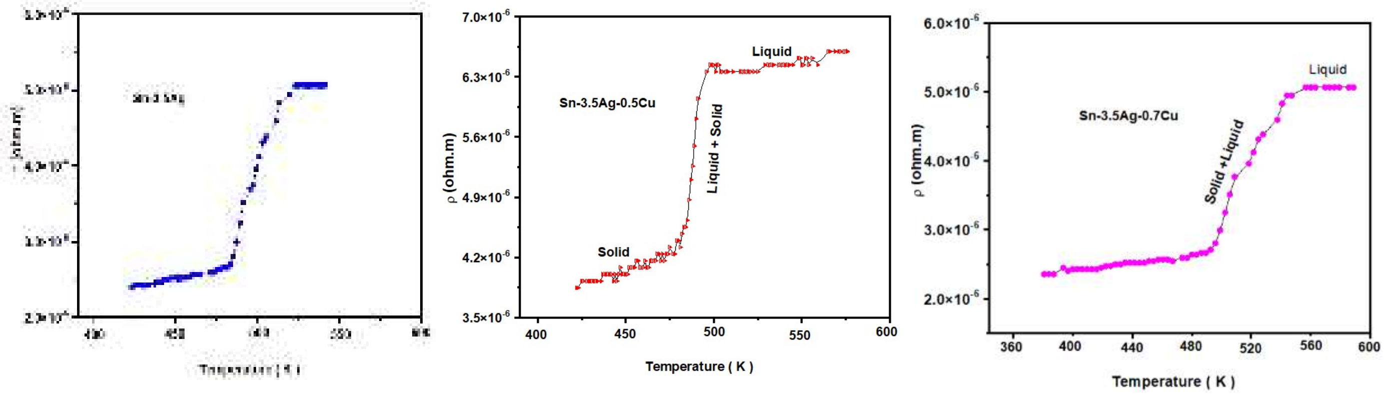


Fig. 4: The electrical resistivity behavior of the prepared samples.

Table 3: Latent Heat (Q) from Resistivity Measurement for Sn solder Alloys.

Solder Alloys	ρ_L/ρ_S	**Q (cal/gm)**	**dρ/dT (Ω.m/deg) Liquid**	**dρ/dT (Ω.m/deg) Solid**
Sn-3.5Ag	2.4	3.51	5.1×10^{-6}	2.5×10^{-6}
Sn-3.5Ag-0.5Cu	3.8	3.91	6.42×10^{-6}	3.81×10^{-6}
Sn-3.5Ag-0.7Cu	6.1	4.51	5.2×10^{-6}	2.5×10^{-6}

The curves in fig. (4) provide a good summary of the electrical resistivity behavior of Sn-Ag-Cu alloys. The temperature of the metal has a distinctive effect on electrical conductivity. Usually, this fluctuation is explained in terms of how resistivity changes with temperature. At temperature ranging from 360 to 470 K ρ has a small approximately constant value; above that, ρ increase with T, slowly at first but then ρ increase linearly with T. The linear behavior continues essentially until the melting point is reached. Scattering takes place in pure crystals because [20] (i) the ion cores vibrating at their equilibrium position at any temperature (ii) the possibility of impurities, or foreign atoms, and (iii) the possibility of lattice flaws in the crystal. The thermal disturbance at higher temperatures can be explained in terms of quantified elastic waves or phonons, and the increase in ρ(T) can be seen as the result of electron-phonon scattering. The high resistivity of Sn-Ag-Cu alloys is linked to the enhanced dispersion of the conduction electrons because of a random atomic arrangement, while the residual resistivity ρ is generated by foreign atoms in solid solution in the matrix metal.

In the current work, residual scattering of the conduction electrons by crystal defects, dislocation, and impurity concentrations governs the solid's resistivity at low temperatures and below the melting point. As the temperature rises, thermal lattice vibrations are also responsible for electron phonon scattering mechanisms, which in turn affect resistivity. All of these "disorder scattering" contributions should rise with melting, and in fact, the resistivity typically doubles in value [19]. However, Mott [23] proposed that the latent heat, Q, of melting might be connected to the ratio of the liquid-to-solid-state resistivities (L/S) using a formula of the following form:

$$Q = \frac{3}{2} k T_m . Ln\left(\frac{\rho_L}{\rho_S}\right) \quad (4)$$

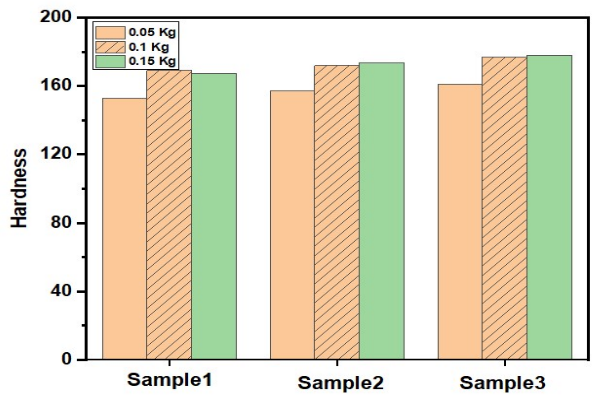
where ρ_L and ρ_S are the resistivities of the sample in the liquid and solid state, respectively, k is the Boltzmann constant, and T_m is the melting point of the sample. The available data [21] indicate incommensurably small additions of metallic impurities on the resistance of liquid metals in comparison with solid materials. This conclusion is confirmed also by the modern quantum electronic theory of liquid metals [20]. Table (3) shows the ratio of the resistivity in the liquid state to that in the solid state (ρ_L/ρ_S) for pure metals and Sn-Ag-Cu alloys. It has been observed experimentally that the total resistivity of a metal is the sum of the contributions from thermal vibrations, impurities, and plastic deformation, that is, the scattering mechanisms act independently of one another. This may be represented in mathematical form as follows:

$$\rho_{total} = \rho_T + \rho_i + \rho_d \quad (5)$$

in which ρ_T, ρ_I, ρ_d represent the individual thermal, impurity, and deformation resistivity contributions, respectively. From resistivity measurements, it is found experimentally that bismuth atoms, as semimetal, act as scattering centers, and increasing the concentrations of bismuth results in an enhancement of resistivity.

3.4 Hardness Measurement

The structural alterations of various soft solders can be detected with high sensitivity using microhardness measurement. It is often non-destructive testing and may be the simplest method to ascertain the mechanical characteristics of the various structural stages. The Vickers hardness number variation of Sn-Ag alloy samples using loads of 0.05, 0.1, and 0.15 kg is displayed in Figure 5.



.

Fig 5: Variation of Vickers hardness

3.5 internal Friction

Alloys that crystallized quickly. It demonstrates how the alloying elements alter the internal friction value. When Ag is added, it rises to its highest value, and when Cu is added, it falls to its lowest value (fig. (6)). This variation can be explained by the dissolving atoms in the Sn-matrix changing into substitutional solid solutions. These solutions have different mobility because of changes in their atomic radii and axial ratios, which can make it more difficult for substitutional atoms to move from one site to another. The internal friction of these alloys changes as a result of the dissolving atoms in the Sn-matrix changing into substitutional solid solutions, which have differing mobilitys because of the shift in their atomic radii.

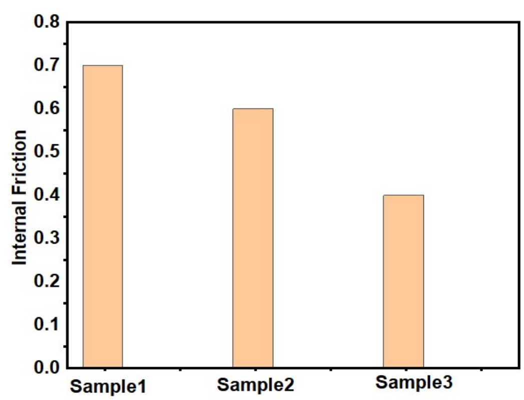
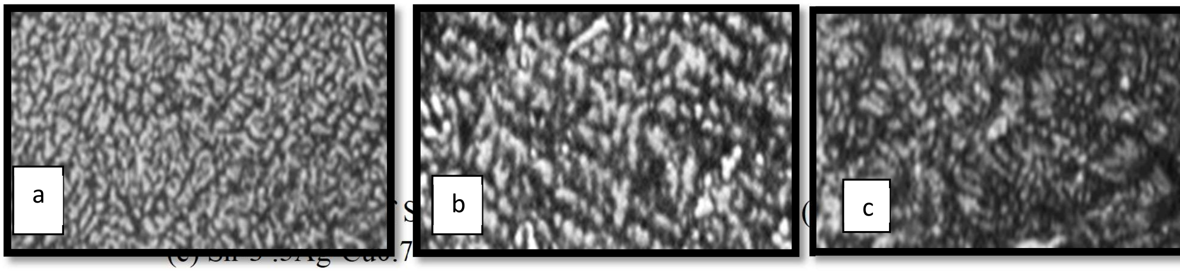


Figure 6: shows the variation of internal friction values of the prepared samples.

3.6 Microstructure

The microstructure of the solder is depicted in Figure (7). Three solder compositions—Sn–3.5Ag, Sn–3.5Ag–0.5Cu, and Sn–3.5Ag–0.7Cu—were selected based on phase equilibria calculations. As the amount of copper in solders grows, their microstructure gets finer and their distribution gets more uniform, as seen in Fig. (7). A tiny quantity of Cu creates an irregular nucleation point, which alters the crystal's growth velocities and different crystallographic orientations. The irregular block-like microstructure of Sn-3.5Ag is seen in Fig. (7a). The crystal grain in Figure 7b is significantly finer than that in Figure 7a when the Cu concentration is 0.5 weight percent. As shown in Fig. (7c), the material has a bar-like or short rod-like shape when the Cu content reaches 0.7 weight percent. The microstructure gets increasingly finer as the Cu content rises. As illustrated in Fig. (7c), the microstructure becomes more homogenous and eutectic as the Cu content rises.



(c) Sn-3.5Ag-Cu0.7

4. Conclusion

The lead-free solder alloys of Sn-3.5Ag, Sn-3.5Ag-0.5Cu, and Sn-3.5Ag-0.7Cu were effectively created in this work by employing the melt-spinning process to quickly solidify Sn-Ag melt. After examining the electrical, thermal, and microstructure characteristics, the following conclusions were drawn.

- The DTA curve was used to determine the distinctive peak temperatures of the Sn–Ag–Cu alloys under investigation, which have a high tin content and a low copper and silver content. DTA curves show that when the alloy's copper content rises, the start and finish of the phase transition are shifted to lower temperatures. They are appropriate for high-reliability component packaging since it has been found that an increase in Cu content lowers the melting point from 221°C to 215°C. With a Pb-free assembly solder, the parts can also be safe for later assembly. These solders typically require an assembly temperature up to 260 °C.
- There was a minor shift in the heat of fusion within the range, with lower values than those of Pb-Sn. Accordingly, Sn-Ag-Cu alloys are thought to be the best material for energy conservation.
- The electrical resistivity, which was discovered to be a very structure-sensitive characteristic, was impacted by the addition of Ag content. The addition of Cu to the rapidly solidified Sn-Ag alloy enhances the properties that make these alloys suitable for soldering technology.
- The addition of Cu to the Sn-Ag alloy improves its mechanical properties by increasing the hardness and internal friction and improving the structure to become finer and more homogeneous.

Credit for author statement

Conceptualization S.E.N.; methodology, investigation, data curation, project administration, review and editing and A.A.B.; resources, supervision and visualization.

Funding
This research received no external funding.
Acknowledgments
The author is grateful to Prof. Dr. A. A. Bahgat Department of physics AL-Azhar University for his continuous support for his students and I am proud to have been mentored by him.

References

[1] Kelly MB, Maity T, Sakib ARN, et al. Influence of substrate surface finish metallurgy on lead-free solder joint microstructure with implications for board-level reliability. J Electron Mater 2020; 49(5): 3251–3258.

[2] Y. Liu and K.N. Tu, Materials Today Advances 8 (2020) 100115

[3] M. Kamal and E. S. Gouda, "Effect of rapid solidification on structure and properties of some lead-free solder al-loy," Materials and Manufacturing Processes, Vol. 21, pp. 736-740, 2006.

[4] Zaneta Gerhátová , Paulína Babincová, Marián Drienovský , Matej Pašák , Ivona Cerniˇckov ˇ á , Libor Duriška , Róbert Havlík and Marián Palcut ,Materials 2022, 15, 7210

[5] Aleksandra Dybeł and Janusz Pstrus,Journal of Materials Engineering and Performance, , 2023, 32:5710–5722

[6] Mahmoud Hammam , Fardos Saad Allah , El Said Gouda, Yaser El Gendy , Heba Abdel Aziz, Engineering, 2010, 2, 172-178

[7] E. S. Gouda, "Effect of cooling rate on structure and creep behavior of Sn-0.7 Cu-0.5 Zn lead-free solder alloy," European Physical Journal: Applied Physics, Vol. 48, pp. 20902-20906, 2009.

[8] R R Kapor and T W Eager, *Metall. Trans.* B20, 919 (1989)

[9] C J Thwaites, *Int. Mater. Rev.* 29, 45 (1984)

[10] M. Kamal and E. S. Gouda, "Effect of rapid solidification on structure and properties of some lead-free solder al-loy," Materials and Manufacturing Processes, Vol. 21, pp. 736-740, 2006.

[11] E. S. Gouda, E. Ahmed and F. Saad Allah, "Electrical and mechanical properties of Sn-5wt.%Sb alloy with an-nealing temperature," European Physical Journal: Ap-plied Physics, Vol. 45, pp. 10901-10905, 2009.

[12] J. Zhao, L. Qi, X. Wang and L. Wang, "Influence of Bi on microstructures evolution and mechanical properties in Sn-Ag-Cu lead-free solder," Alloys and Compounds, Vol. 375, pp. 196, 2004

[13] R. Islam, B. Wu, M. Alam, Y. Chan and W. Jillek, "In-vestigations on microhardness of Sn-Zn based lead-free solder alloys as replacement of Sn-Pb solder," Alloys and Compounds, Vol. 392, pp. 149-158, 2005.

[14] Samia E. Attia Negm, A.S. Abdel Moghny and Syed Ismail Ahmad "Investigation of thermal and mechanical properties of Sn-Zn and Sn-Zn- Bi near-eutectic solder alloys, Results in Materials, 15, 100316,2022.

[15] J. Zhao, L. Qi, X. Wang and L. Wang, "Influence of Bi on microstructures evolution and mechanical properties in Sn-Ag-Cu lead-free solder," Alloys and Compounds, Vol. 375, pp. 196, 2004.

[16] M. Kamal and E. S. Gouda, "Enhancement of solder properties of Sn-9Zn lead-free solder alloy," Crystal Re-search and Technology, Vol. 41, No. 12, pp. 1210-1213, 2006.

[17] J.Y. Park, J.S. Ha, C.S. Kang, K.S. Shin, M.H. Kim, and J.P. Jeong, J. Electron. Mater. 29, 1145 (2000).

[18] Ziman, J. M. " The Physics of Metals" Cambridge Unv. Press, London, (1969).

[19] M. M. El-Bahay, S. S. Negm and A.A.Bahgat, Radiation Effects & Defects in Solids, Vol. 159, Pages 381-391, (2004).

[20] M. Kamal, A.B.El-Bediwi, J. of Materials Science: Materials Electronics, Vol. 9, Pages 425-428, (1998).

[21] Prokhorebko, V. Ya., Ratushnyak, E. A., Staydnyk, B. I., Lakh, V. I. And Korsunskii, M. Teplofizika Vysokikh emperature, English Translation 7(4), 804, (1969).

[22] Avakyan, S.V. and Lashka, N. F. Doklady, Akad. Nauk. USSR, 65, 29, (1946).

[23] P.T. Viaco and J.A. Rejent, J. Electron. Mater., 28, 1138 (1999).

[24] S. N. Salama and H. A. El-Batal, J. of Non-Cryst. Solids, 168, 179 (1994).