Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi
Afyon Kocatepe University Journal of Science and Engineering

AKÜ FEMÜBİD **22** (2022) 031101 (477-485) AKU J. Sci. Eng. **22** (2022) 031101 (477-485)
DOI: 10.35414/akufemubid.1075864

Araştırma Makalesi / Research Article

Mechanical and Microstructural Properties of In, Ag, Al Doped Lead-Free Sn-Zn Solder Alloy Systems

Esra ÖZTÜRK
Kocaeli University, Department of Physics, 41380 Kocaeli, Turkey.

e-posta: esra.ozturk@kocaeli.edu.tr ORCID ID: https://orcid.org/0000-0002-3531-7564

Geliş Tarihi: 18.02.2022 Kabul Tarihi: 09.05.2022

Keywords
Lead-free solder systems; Mechanical properties; Microstructure; Differential Scanning Calorimetry; Microhardness

Abstract

Sn-Zn based lead free alloys are considered for replacing lead containing alloy systems for soldering. In this paper, In, Ag, Al doped Sn-Zn based systems were produced and investigated for mechanical and microstructural properties to obtain the most suitable system. Microstructures were observed by using an optic microscope. The samples' existing phases were investigated by using Energy Dispersive X-Ray analysis (EDX). Melting temperatures, the enthalpy of fusion and the specific heat change between the liquid and solid phases in the systems were determined with Differential Scanning Calorimetry (DSC). Also, microhardness values were measured at room temperature.

In, Ag, Al Katkılı Kurşunsuz Sn-Zn Lehim Alaşım Sistemlerinin Mekanik ve Mikroyapısal Özellikleri

Anahtar kelimeler
Kurşunsuz Lehim Sistemleri; Mekanik Özellikler; Mikroyapı; Diferansiyel Taramalı Kalorimetre; Mikrosertlik

Öz

Sn-Zn bazlı kurşunsuz alaşımlar, lehimleme için kurşun içeren alaşım sistemlerinin yerine kullanılmak üzere düşünülmektedir. Bu çalışmada, In, Ag, Al katkılı Sn-Zn esaslı sistemler üretilmiş ve en uygun sistemin elde edilmesi için mekanik ve mikro yapısal özellikler incelenmiştir. Mikro yapılar bir optik mikroskop kullanılarak gözlemlenmiştir. Numunelerin mevcut fazları Enerji Dağılım X-Işını Spektrometresi (EDX) kullanılarak araştırılmıştır. Sistemlerdeki erime sıcaklıkları, füzyon entalpisi ve sıvı ve katı fazlar arasındaki özgül ısı değişimi Diferansiyel Taramalı Kalorimetre (DSC) ile belirlenmiştir. Ayrıca oda sıcaklığında mikrosertlik değerleri de ölçülmüştür.

1. Introduction

Solder systems are used in many fields of industry and electronic technology all over the world for hundreds of years. After serious harmful effects of lead on human health and environment had been proven, scientists were performed considerable number of studies (Mc Cormack *et al*. 1993, Ghosh *et al*. 1994, Mc Cormack and Jin 1994, Lee *et al*. 1997, Abtewa and Selvaduray 2000, Suganuma 2001, Xing and Qiu 2015, Xing *et al*. 2015, Doğan and Arslan 2018, Doğan and Arslan 2019, Doğan and Arslan 2018, Li *et al*. 2020, Rashidi and Naffakh-Moosavy 2021) about lead-free systems. Besides, soldering research continued to be up to date because of their usage area in junctions, metal works, many parts of electronic devices etc. Related to this, lead-free systems were gain importance in soldering technology. However, efforts to obtain lead-free solder that can replace the traditional Tin-Lead (Sn-Pb) system are continuing. At this point it is thought that Sn-9Zn (Tin-9Zinc) solder system may be a good candidate for soldering because of their similar mechanical properties and especially similar melting temperature.

In soldering technology, Sn component is useful for making stronger bonds during soldering process. Besides, Sn-Zn system has perfect mechanical properties (Mc Cormack *et al*. 1993, Ghosh *et al*. 1994, Mc Cormack and Jin 1994, Mc Cormack *et al*. 1994, Kattner and Boettinger 1994, Loomans *et al*. 1994, Artaki *et al*. 1994, Kang and Sarkhel 1994, Mc Cormack and Jin 1994, Wood and Nimmo 1994). Indium (In) addition is providing many advantages such as good wettability, fatigue resistance to the system (Mei and Morris 1992). In addition, small amount of Ag addition affects the mechanical properties positively by dispersing. Al prevents the atmospheric corrosion and assists the system in many ways like strength, formability, conductivity.

For these purposes the aim of this study was to investigate the microstructural and mechanical properties of 1 wt.% In, Ag, Al doped Sn-9Zn lead-free solder alloy systems and to find the most proper system for the next research. Additionally, this will be good for scientists and engineers who will use this alloy systems.

2. Experimental Process

2.1. Sample production

In, Ag, Al doped Sn-9Zn solder systems were obtained by using metals that have 99.99 wt.% purity. For tensile strength measurements 50x6 mm graphite sample pots and for microstructure and DSC analysis and microhardness measurements, 50x12 mm graphite pots were used. About 25 cm3 of metal was melted in a graphite crucible by using a vacuum melting furnace which provided no oxidations in melting process. After melting process, the molten alloy was stirred well and filled to another crucible for directionally solidification in a special filling furnace (Gündüz and Hunt 1985, and Maraşlı and Hunt 1996). After solidification, the samples were left for cooling. After cooling process, they were removed from the crucible and cut transversally into 5 mm in length and 8 mm in diameter with a Micracut 151 cutting device. By using a transparent thermoplastic resin, the cut samples were mounted. The samples were ground flat with 180 grit SiC gritting paper and polished by using a Struers TetraPol-15 automatic machine. Before each polishing step the samples were washed with a soap solution and then cleaned ultrasonically for 5 minutes. After all, the samples were cleaned by using ethanol and etched with 20 ml Glyserin, 2.5 ml Acetic Acid and 2.5 ml Nitric Acid solution for 10 seconds to see the microstructure clearly.

2.2. Microstructure and chemical composition

Microstructure analyses were performed by using a Nikon Eclipse MA 100 type optical microscope. The existing phases were identified by Energy Dispersive X-Ray (EDX) analysis. EDX determines the elemental composition of an area, with a sensitivity of perhaps 0.1 to 1 percent composition. EDX is commonly used for elements with atomic number greater than 11 (Marshall 1991). Quantitative chemical composition analysis results and microstructure photographs were given in Fig. 1 together.

2.3 Measurement of Microhardness

Microhardness measurement is one of the most important techniques applied to understand the mechanical properties of materials. Since the measurement of microhardness is harmless and simple for the material, it contributes to a preliminary study of which processes can be applied without spending the amount of sample (Callister and Rethwisch 2008).

In this paper, Vickers method was used for the microhardness measurements. Vickers Pyramid Number (HV) is calculated from the equation below which is known as the unit of microhardness.

$$\mathrm{HV} = 1.8544\left(\frac{\mathrm{F}}{\mathrm{D}^2}\right) \quad (1)$$

Here F (kgf) is the applied load and D (mm) is the area of the indentation (Callister and Rethwisch 2008). In this study the measurements were made by using a Future-Tech FM-700 model hardness measuring device using a 10 g to 50 g load and dwell time of 10 s, giving a typical indentation depth of about 40 to 60 µm. Microhardness values of the samples were found with calculating the average of 10 measurements on the transverse sections and given in Fig. 2 and Table 1.

2.4 The enthalpy of fusion and the specific heat change for liquid to solid transformation

Differential scanning calorimetry (DSC) is a thermoanalytical method used for the thermal analysis. DSC measures the amount of absorbed or released energy, when the sample is heated, cooled, or kept at a constant temperature. In the method, the temperature difference coming or away from the sample is measured depends on the process temperature and time (Aksöz et.al. 2021).

In the present study, In, Ag, Al doped Sn-Zn based lead free solder systems were heated with a Perkin Elmer Diamond model DSC with a heating rate of 10 K/min up to 573 K. In Fig. 3, the variations of heat flow with temperature are shown.

The specific heat of a material at a constant pressure can be given as

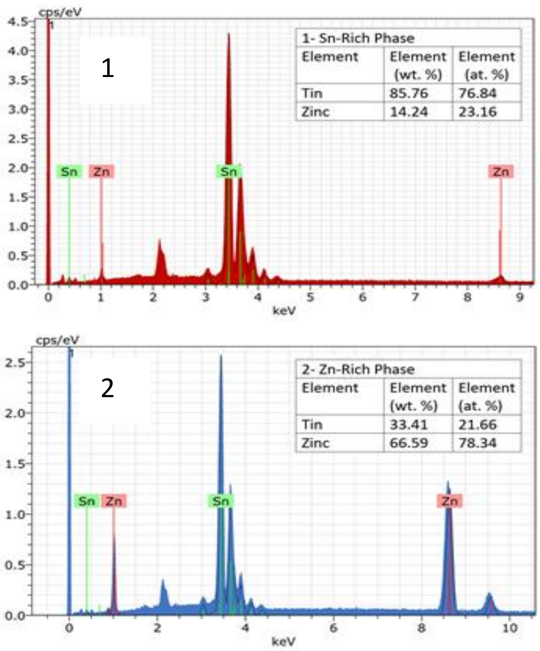
$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{2}$$

By integration of Eq. (2), the enthalpy of a material, by defining H=0 at 298 K, can be obtained as

$$H = \int_{298}^{T} C_p dT \tag{3}$$

The heat given to the system at the melting point will not raise its temperature. This heat has called enthalpy of fusion or latent heat of melting and used to transform from solid to liquid. The enthalpy of fusion can be given as;

$$\Delta H \approx \Delta C_p T_M \tag{4}$$



where T_M is the melting temperature, ΔCP is the specific heat difference between liquid and solid phases (Powers 2010).

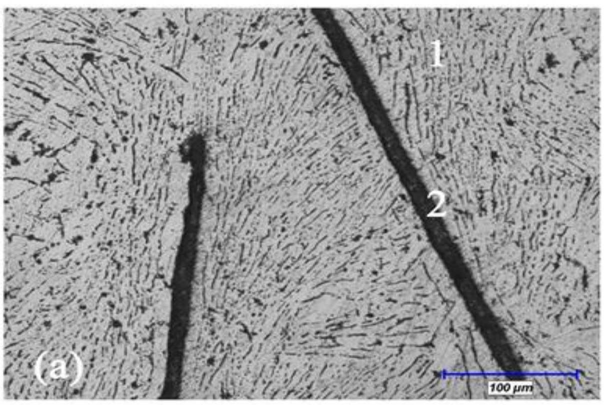
3. Results and discussion

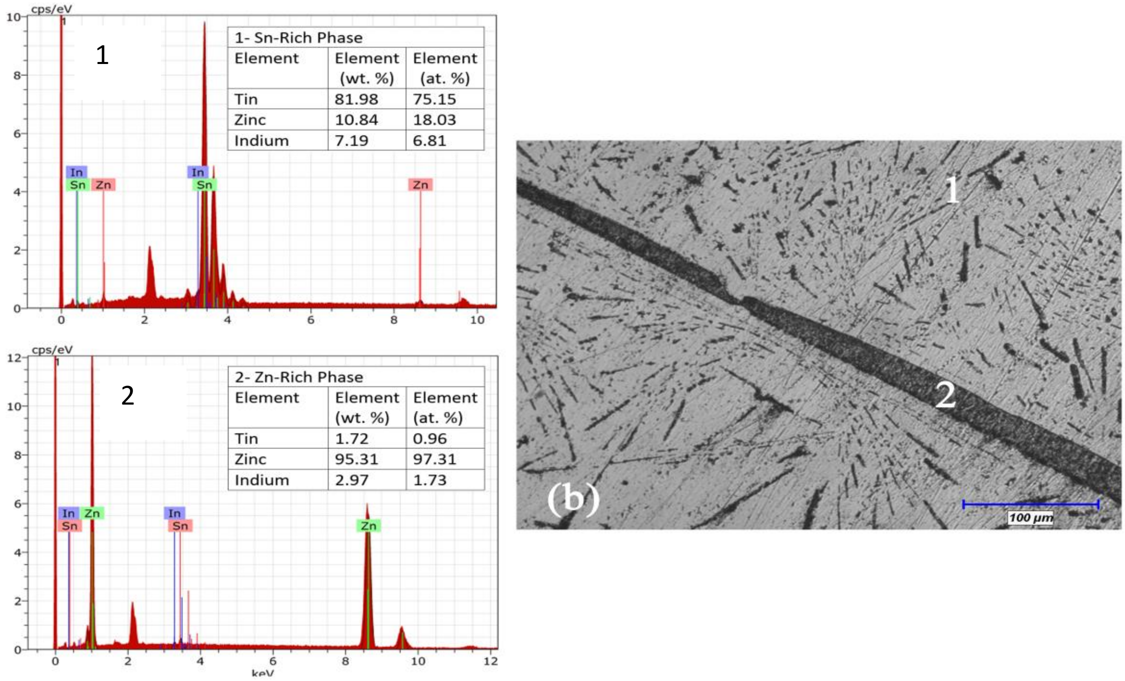
3.1. The Microstructure of the Samples

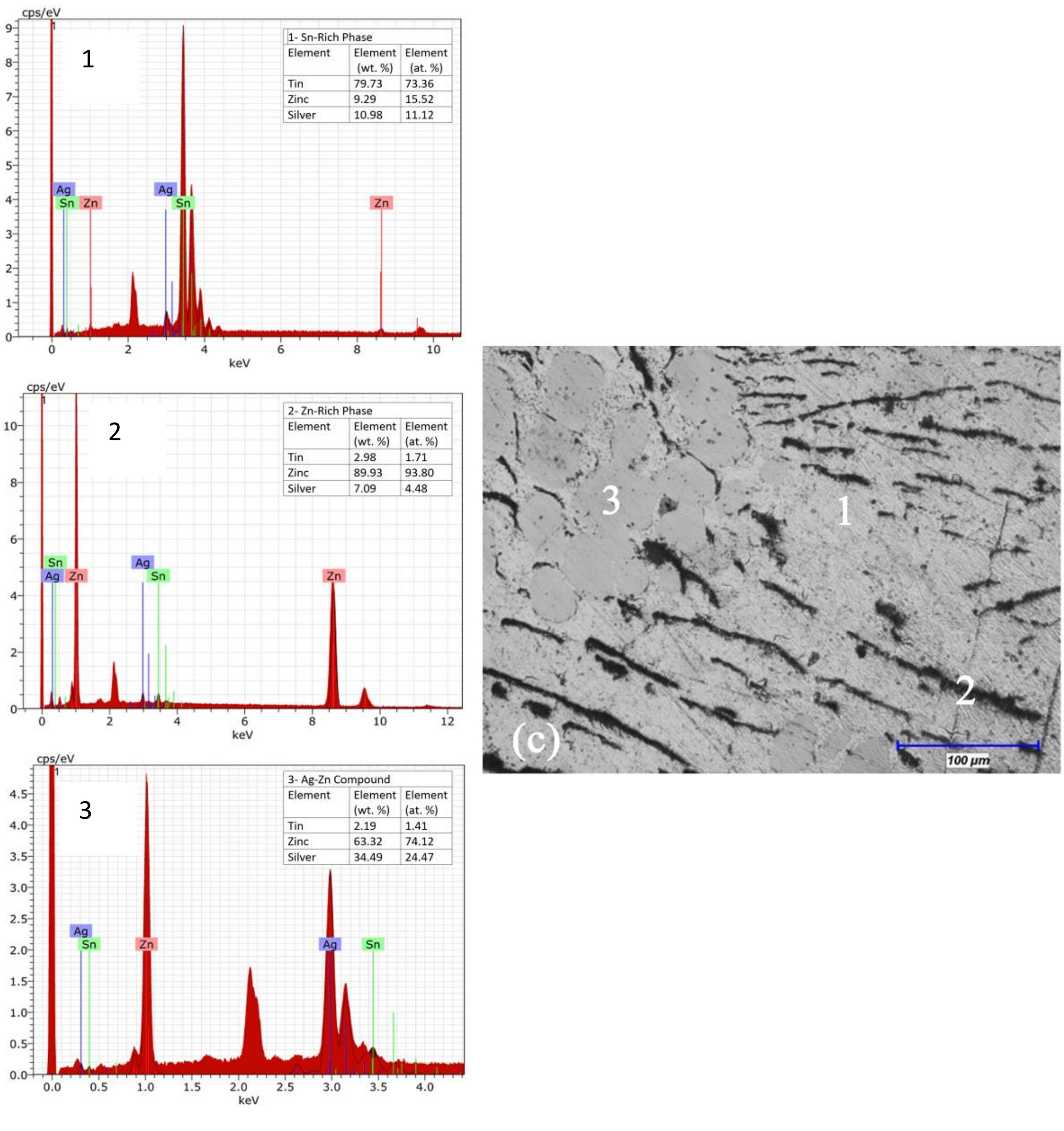
Fig. 1 shows the optical microscope images taken to examine the microstructures of each alloy system and EDX spectrometer graphics used to determine the elemental composition analysis of Sn-9Zn and In, Ag, Al doped Sn-9Zn solder systems. As in the Sn-9Zn alloy system, two different phases, Sn-rich and rod-shaped Zn-rich, were observed in In and Al doped Sn-9Zn alloy systems. In addition to the Sn-rich and Zn-rich phases, a third phase was obtained in the Ag doped Sn-9Zn alloy system called Ag-Zn compound (Hung *et al*. 2006). In addition, when the microstructure photographs were examined, it was seen that these contributions to the Sn-9Zn alloy system did not cause much change in the structure of the phases as seen in Fig. 1.

3.2. Change of Microhardness Value According to Doping Material

In solder systems, dislocation motion, growth, and configuration of the grains effect microhardness value directly. In Sn-based solder systems microhardness is strongly dependent on the alloying elements (Kang *et al*. 2021). In this study, microhardness test was performed to observe the change of mechanical properties with microstructural changes. The results of microhardness as a function of alloy composition were given in Fig. 2 and the values were given in Table 1.




1- Sn-Rich Phase
Element | Element (wt. %) | Element (at. %)
Tin | 81.98 | 75.15
Zinc | 10.84 | 18.03
Indium | 7.19 | 6.81
2- Zn-Rich Phase
Element | Element (wt. %) | Element (at. %)
Tin | 1.72 | 0.96
Zinc | 95.31 | 97.31
Indium | 2.97 | 1.73
(b)
100 µm


1- Sn-Rich Phase
Element | Element (wt. %) | Element (at. %)
Tin | 79.73 | 73.36
Zinc | 9.29 | 15.52
Silver | 10.98 | 11.12
2- Zn-Rich Phase
Element | Element (wt. %) | Element (at. %)
Tin | 2.98 | 1.71
Zinc | 89.93 | 93.80
Silver | 7.09 | 4.48
3- Ag-Zn Compound
Element | Element (wt. %) | Element (at. %)
Tin | 2.19 | 1.41
Zinc | 63.32 | 74.12
Silver | 34.49 | 24.47
(c)
100 µm

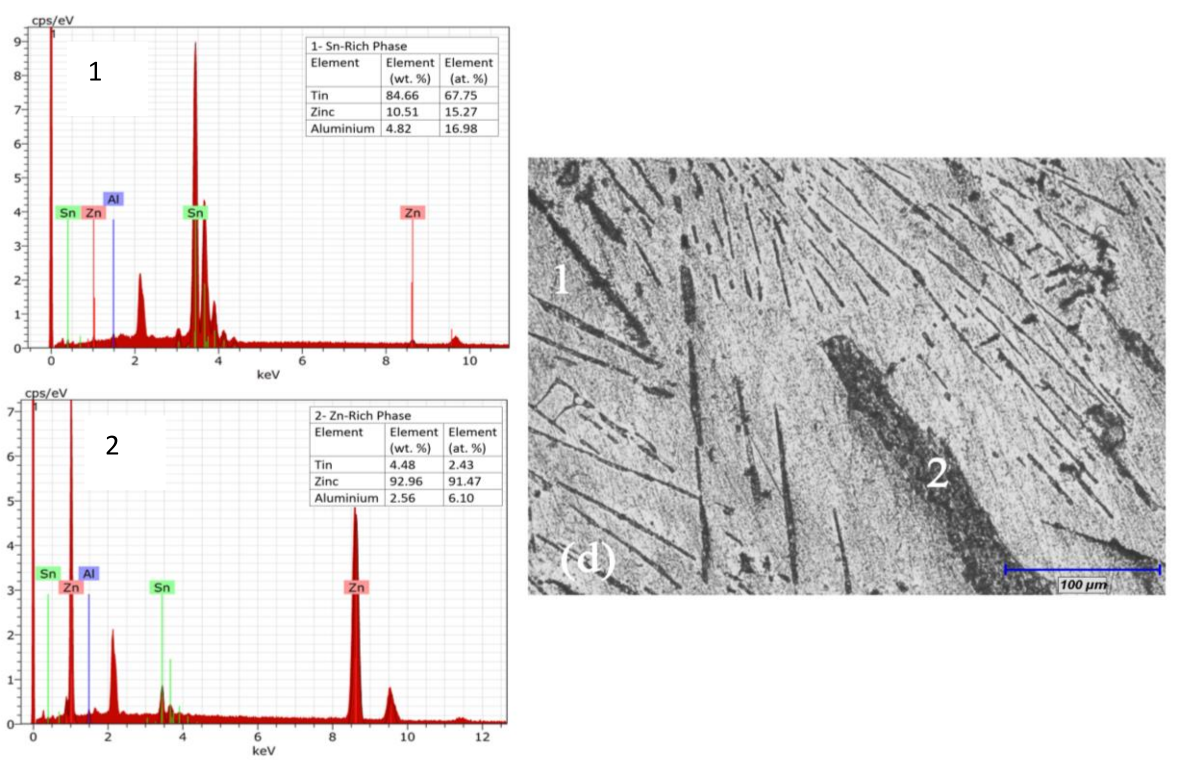


Figure 1. Optic microscope photographs and EDX analysis results of (a) Sn-9Zn (b) In-doped Sn-9Zn, (c) Ag-doped Sn-9Zn and (d) Al-doped Sn-9Zn alloy systems.

In the tin-dominated matrix phase, microhardness values were taken from 10 different regions for 10 seconds with 50 g load. The microhardness values of In, Ag and Al, metals doped to the Sn-9Zn alloy system are 8.83 kg/mm^2 (Samsonov 1968), 94.57 kg/mm^2 (El-Bahay *et al*. 2004) and 30.05 kg/mm^2 (Sivasankaran *et al*. 2021) respectively.

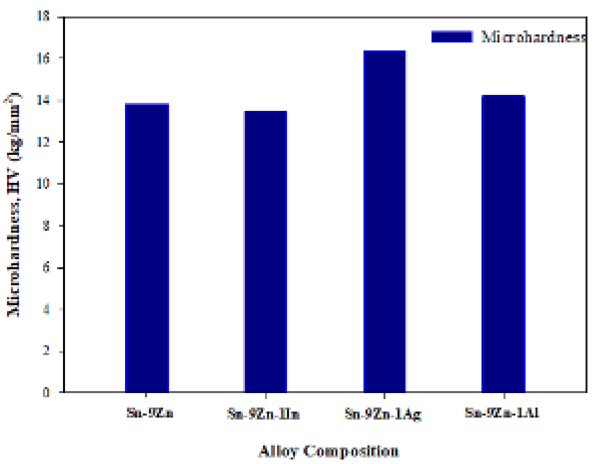


Figure 2. Microhardness values of Sn-9Zn, Sn-9Zn-1In, Sn-9Zn-1Ag, Sn-9Zn-1Al solder alloys.

For Sn-9Zn and 1 wt.% In, Ag, Al doped Sn-9Zn alloy systems, the microhardness values were obtained as 13.83 kg/mm^2, 13.49 kg/mm^2, 16.36 kg/mm^2 and 14.26 kg/mm^2 respectively. As seen from the results, the average microhardness value increased by Ag and Al doping for Sn-9Zn alloy system but decreased by In, as expected. Thus, it was concluded that Sn-9Zn-1Ag system, might be a candidate as an alternative solder system, has better mechanical properties.

Table 1. Results of microhardness tests of Sn-9Zn, Sn-9Zn-1In, Sn-9Zn-1Ag, Sn-9Zn-1Al solder alloy systems.

Composition (wt.%)	Microhardness HV (kg·mm^{-2})
Sn-9Zn	13.83
Sn-9Zn-1In	13.49
Sn-9Zn-1Ag	16.36
Sn-9Zn-1Al	14.26

3.3. The Enthalpy of Fusion and The Specific Heat Change of Material

Heating curves are very practical to determine the reaction temperatures of the materials. The peaks in the reactions indicate endothermic reactions associated with heat absorption during melting. Initial temperature of the reaction is T_{onset}, the starting point of the endothermic peak. T_{end} is the final temperature of the endothermic peak. After heating, the T_{onset} is solidification temperature and Tend point is liquidus temperature of the alloys (Chou and Chen 2006]. The heating curves of Sn-9Zn and 1 wt.% In, Ag, Al doped Sn-9Zn alloy systems during heating with heating rate 10 K/min. obtained by Differential Scanning Calorimetry (DSC) are shown in Fig. 3 and the values obtained from the graphs are given in Table 2.

From Fig. 3 the solidus temperature T_S, liquids temperature T_L and enthalpy (ΔH) are calculated and presented in Table 2.

Another significant issue is the heat fusion of the alloy systems. From Table 2, it is seen that the enthalpy values are 69.12, 46.27, 60.75 and 72.84 J/g for Sn-9Zn and 1 wt.% In, Ag, Al doped Sn-9Zn alloy systems, respectively. The specific heat values calculated from the DSC peaks of the alloys were given in Table 2.

From the results, the intermetallic compound with the lowest energy storage capacity is Sn-9Zn-1In alloy system with the value of 0.2331 J/g°C. Also, as can be seen from Table 2, doped elements decreased the melting temperature of Sn-9Zn alloy system.

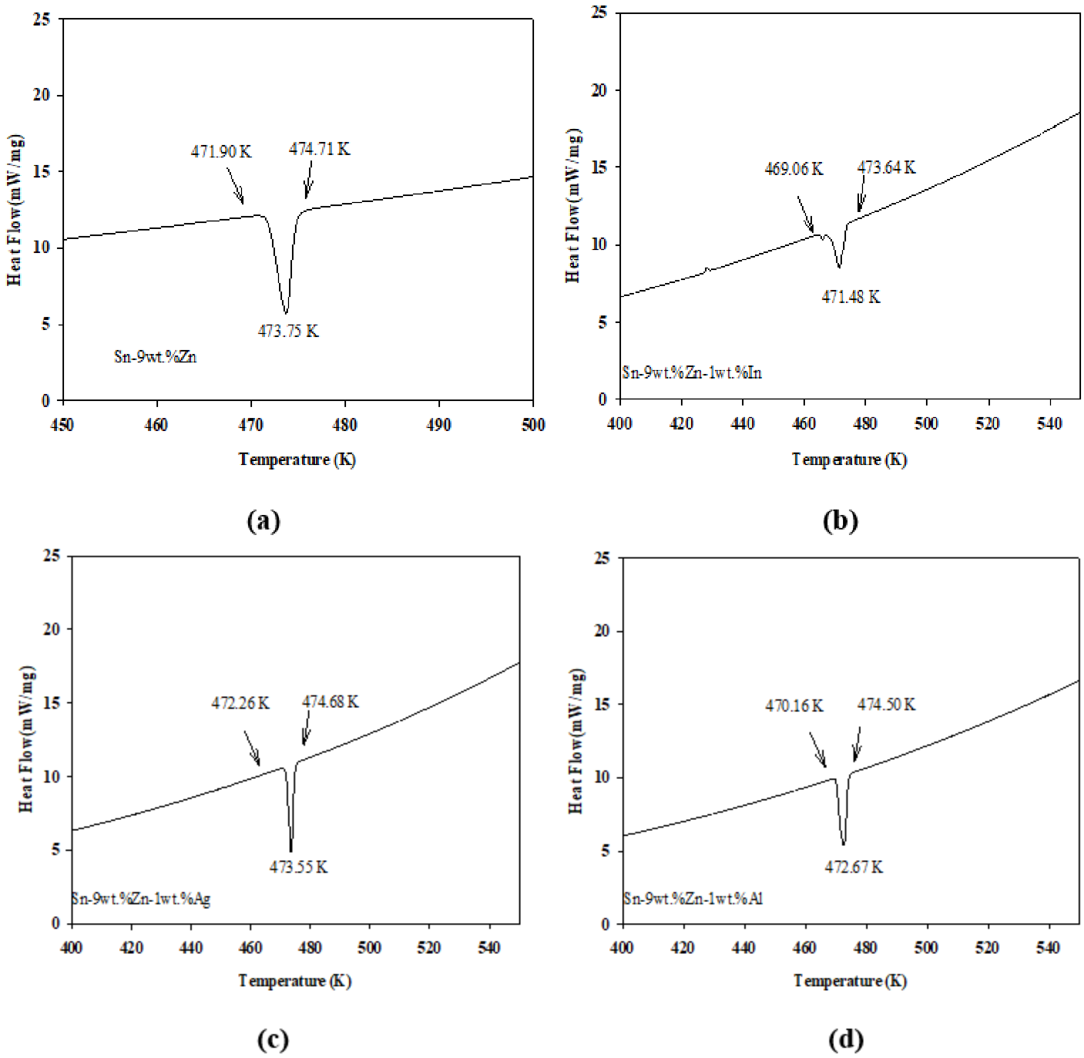


Figure 3. DSC thermogram of (a) Sn-9Zn, (b) 1 wt. % In doped Sn-9Zn, (c) 1 wt.% Ag doped Sn-9Zn, (d) 1wt.% Al doped Sn-9Zn lead-free solder alloy system at heating rates of 10 ^{0}C/min.

Table 2. The specific heat and the enthalpy values for the 1 wt. % In, Ag, Al doped Sn-9Zn lead-free solder alloy systems.

Composition (wt. %)	Solidus Temperature (K)	Liquids Temperature (K)	Peak Temperature (K)	Enthalpy (J/g)	Specific Heat (J/gK)
Sn-9Zn	471.90	474.71	473.75	69.12	0.3443
Sn-9Zn-1In	469.06	473.64	471.48	46.27	0.2331
Sn-9Zn-1Ag	472.26	474.68	473.55	60.75	0.3029
Sn-9Zn-1Al	470.16	474.50	472.67	72.84	0.3648

4. Conclusions

For many reasons, explained in the previous parts, four different compositions, Sn-9Zn and 1 wt.% In, Ag, Al doped Sn-9Zn alloy systems' thermal, microstructural, and mechanical properties were investigated by using the described methods to find the alternative solder alloy system. The results were explained and commented in the whole paper. The study was focused more than one point to obtain the optimal soldering alloy system. From the results and comparisons with the studies in the literature, it is clearly seen that this system will be useful and hopeful in the usage area. After experiments it was aimed to provide convenience to the scientists and engineers in choosing materials in further studies. The results are listed below. As a summary, the results are listed below.

1. From composition analysis results, two different phases, Sn-rich and Zn-rich, were obtained for all systems except Ag doped system. In Ag doped Sn-9Zn system, in addition to these two phases, a third phase, Ag-Zn compound, was also observed. From the microstructure photographs, it was seen that the additions made to the Sn-9Zn alloy system did not cause much change in the structure of the phases.

2. Microhardness values of the alloys systems were examined; it was observed that average microhardness value increases by Ag and Al doping for Sn-9Zn alloy system but decreased by In. Thus, it was determined that the mechanical properties of Sn-9Zn-1Ag system was more suitable than the other doped systems.

3. The melting temperatures, the enthalpy of fusion and the specific heat change of Sn-9Zn and 1 wt.% In, Ag, Al doped Sn-9Zn alloy systems were determined by using DSC. From the results, the intermetallic compound with the lowest energy storage capacity is Sn-9Zn-1In alloy system with the value of 0.2331 J/g°C. As seen from Table 2, doped elements decreased the melting temperature of Sn-9Zn alloy system.

Acknowledgments

I'd like to thank to Scientific Research Project Unit of Nevsehir Hacı Bektas Veli University for their funding.

References

Abtewa M., Selvaduray G., 2000. Lead-free Solders in Microelectronics. *Materials Science and Engineering: R: Reports,* **27(5),** 95-141.

Aksöz S., Ata Esener P., Öztürk E., Maraslı N., 2021. Effects of Bi content on thermal, microstructure and mechanical properties of Sn-Bi-In-Zn solder alloy systems. *Journal of Materials Science: Materials in Electronics*, **33(9)**, 11-26.

Artaki I., Jackson A.M., Vianco P.T., 1994. Evaluation of Lead- Free Solder Joints in Electronic Assemblies. *Journal Of Electronic Materials*, **23(8),** 757-764.

Callister W.D., Rethwisch D.G., 2008. Materials Science and Engineering an Introduction, 8th ed., John Wiley & Sons, Inc., 175.

Chou C.Y., Chen S.W., 2006. Phase equilibria of the Sn–Zn–Cu ternary system. *Acta Materialia.* **54**, 2393–2400.

Doğan A., Arslan H., 2019. An investigation of influencing of Sb and Bi contents on surface tensions associated with Pb-free Sn-Zn-Sb-Bi quaternary and sub-quaternary solder alloys. *Philosophical Magazine*. **99(15)**, 1825-1848.

Doğan A., Arslan H., 2018. Assessment of Thermodynamic Properties of Lead-Free Soldering Co-Sb-Sn, Ag-In-Pd-Sn, and Ni-Cr-Co-Al-Mo-Ti-Cu Alloys. *Physics of Metals and Metallography*. **119(10**), 976-992.

Doğan A., Arslan H., 2018. Thermophysical properties of Cu–In–Sn liquid Pb-free alloys: viscosity and surface tension. *Philosophical Magazine*. **98(1)**, 37-53.

El-Bahay M.M., El Mossalamy M.E., Mahdy M., Bahgat A.A., 2004. Some Mechanical Properties of Sn-3.5Ag eutectic alloy at different temperatures, *Journal of Materials Science: Materials in Electronics*, **15**, 519-526.

Ghosh G., Loomans M., Fine M.E., 1994. An Investigation of Phase Equilibria of the Bi-Sb-Sn System. *Journal Of Electronic Materials,* **23(7)**, 619-624.

Gündüz M., Hunt J.D., 1985. The measurement of solid−liquid surface energies in the Al−Cu, Al− Si and Pb−Sn systems. *Acta Metallurgica,* **33**, 1651–1672.

Hung Y., Wang C.J., Huang S.M., Chen L.H., Lui T.S., 2006. Thermoelectric characteristics and tensile properties of Sn–9Zn–xAg lead-free solders. *Journal of Alloys and Compounds,* **420**, 193–198.

Kang H., Rajendran S.H., Jung J.P., 2021. Low melting temperature Sn-Bi solder: effect of alloying and nanoparticle addition on the microstructural, thermal, interfacial bonding, and mechanical characteristics. *Metals*, **11**, 364-388.

Kang S.K., Sarkhel A.K., 1994. Lead (Pb)-free solders for electronic packaging. *Journal Of Electronic Materials*, **23(8)**, 701-707.

Kattner U.R., Boettinger W.J., 1994. On the Sn-Bi-Ag Ternary Phase Diagram. *Journal Of Electronic Materials*, **23(7)**, 603-610.

Lee B.J., Hwang N.M., Lee H.M., 1997. Prediction of interface reaction products between Cu and various solder alloys by thermodynamic calculation. *Acta Materialia*, **45(5)**, 1867-1874.

Li Y., Chen C., Yi R., Ouyang Y., 2020. Review: Special brazing and soldering. *Journal of Manufacturing Processes*, **60,** 608-635.

Loomans M.E., Vaynman S., Ghosh G., Fine M.E., 1994. Investigation of Multi-Component Lead-free Solders. *Journal Of Electronic Materials*, **23(8)**, 741-746.

Maraşlı N., Hunt J.D., 1996. Solid−liquid surface energies in the Al−$CuAl_2$, Al−$NiAl_3$ and Al− Ti systems, *Acta Metallurgica*, **44**, 1085–1096.

Marshall J.L., 1991. Scanning Electron Microscopy and Energy Dispersive X-ray (SEM/EDX) Characterization of Solder Solderability and Reliability, Springer Science+Business Media, New York, 173.

Mc Cormack M., Jin S., 1994. New Lead-Free Solders *Journal of Electronic Materials,* **23(7)**, 635-640.

Mc Cormack M., Jin S., 1994. Improved mechanical properties in new Pb-free solder alloys. *Journal Of Electronic Materials*, **23(8),** 715-720.

Mc Cormack M., Jin S., Kammlott G.W., Chen H.S., 1993. New Pb-free solder alloy with superior mechanical properties. *Applied Physics Letters*, **63**, 15.

Mc Cormack M., Jin S., Chen H.S., Machusak D.A., 1994. New Lead-Free, Sn-Zn-In Solder Alloys. *Journal Of Electronic Materials*, **23(7)**, 687-690.

Mei Z., Morris J.W., 1992. Superplastic Creep of Low Melting Point Solder Joints. *Journal Of Electronic Materials,* **21(4)**, 401-407.

Powers J.M., 2010. Department of Aerospace and Mechanical Engineering University of Notre Dame, USA, 124, 130, 135.

Rashidi R., Naffakh-Moosavy H., 2021. Metallurgical, physical, mechanical and oxidation behavior of lead-free chromium dissolved Sn–Cu–Bi solders. *Journal of Materials Research and Technology*, **13**, 1805-1825.

Samsonov G.V., 1968. Mechanical Properties of the Elements, Handbook of the physicochemical properties of the elements. IFI-Plenum, New York, USA.

Sivasankaran S., Ramkumar K.R., Ammar H.R., Al-Mufadi F.A., Alaboodi A.S., Irfan O. M., 2021. Microstructural evolutions and enhanced mechanical performance of novel Al-Zn die-casting alloys processed by squeezing and hot extrusion, *Journal of Materials Processing Technology*. **292**, 117063.

Suganuma K., 2001. Advances in lead-free electronics soldering. *Current Opinion in Solid State & Materials Science*, **5**, 55–64.

Wood E.P., Nimmo K.L., 1994. In search of new lead-free electronic solders. *Journal Of Electronic Materials*, **23(8)**, 709-713.

Xing F., Qiu X., 2015. Thermal Properties, Electrochemical Behavior, and Microstructure of Zn-5Sn-2Cu-1.5Bi-xRE High-Temperature Solder. *Journal of Materials Engineering and Performance*, **24**, 1679-1686.

Xing F., Qiu X.M., Li Y.D., 2015. Effects of Sn element on microstructure and properties of Zn–Cu–Bi–Sn high-temperature solder. *Transactions of Nonferrous Metals Society of China*, **25(3),** 879-884.