Article

Modelling the Effect of Cu Content on the Microstructure and Vickers Microhardness of Sn-9Zn Binary Eutectic Alloy Using an Artificial Neural Network

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Abstract: The present study aims to clarify the impact of Cu addition and aging conditions on the microstructure development and mechanical properties of Sn-9Zn binary eutectic alloy. The Sn-9Zn alloys with varying Cu content (0, 1, 2, 3, and 4 wt.%) were fabricated by permanent mold casting. X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were utilized to investigate the influence of Cu concentration on the microstructure of pre-aged Sn-9Zn-Cu alloys. The main phases are the primary β -Sn phase, eutectic α -Zn/ β -Sn phases, and γ -Cu₅Zn₈/ η -Cu₆Sn₅/ ϵ -Cu₃Sn intermetallic compounds. Vickers microhardness values of Sn-9Zn alloys increased with additions of 1 and 2 wt.% Cu. When the concentration of Cu exceeds 2 wt.%, the values of microhardness declined. Besides, the increase in the aging temperature caused a decrease in the microhardness values for all the investigated alloys. The variations in the microhardness values with Cu content and/or aging temperature were interpreted on the basis of development, growth, and dissolution of formed phases. The alterations of the lattice strain, dislocation density, average crystallite size, and stacking fault probability were evaluated from the XRD profiles of the investigated alloys. Their changes with Cu content and/or aging temperature agree well with the Vickers hardness results. An artificial neural network (ANN) model was employed to simulate and predict the Vickers microhardness of the present alloys. To check the adequacy of the ANN model, the calculated results were compared with experimental data. The results confirm the high ability of the ANN model for simulating and predicting the Vickers microhardness profile for the investigated alloys. Moreover, an equation describing the experimental results was obtained mathematically depending on the ANN model.

Keywords: Pb-free solders; Vickers hardness; ANN model; microstructure; copper content

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1. Introduction

Due to the inherent toxicity of Sn-Pb solders to human health and environmental considerations, increasing efforts have been made to develop new Pb-free solders with low melting point, low cost, good corrosion resistance, good wettability, and high electrical conductivity with reasonable mechanical properties [1,2]. The establishment of near-eutectic Sn-3.0Ag-0.5Cu (SAC305) alloy has marked the beginning of Pb-free solder alloy development in the electronic packaging industry [3,4]. SAC305 alloy is widely used by the industry as the most promising candidate for reliable Pb-free solder due to its thermal reliability [5,6]. However, there are certain shortcomings of SAC305 solder alloys. For instance, the melting temperature of SAC305 alloy is 217 °C, which is more than 30 °C higher than that of the conventional Sn-37Pb (183 °C) [7]. Some temperature sensitive components, such as optoelectronic elements, cannot withstand such high temperature during reflow processing, thereby limiting the wider application of SAC305 solder alloys in the electronics industry [3]. Second-generation alloys with lower Ag content have been

developed and implemented to enhance the mechanical shock resistance of solder joints [6]. Research has been driven by the varying reliability performance of SAC based alloys under different stimuli, such as impact, vibration and thermo-mechanical loading, the results of which indicate that there is no one substitute for tin-lead solder and that alloy choice may be application specific [8]. In response to complex new manufacturing and high reliability requirements, such as automotive, telecommunication, mission-critical aeronautics, military, and medical applications, where high operating temperatures, rapid thermal and power cycles, long dwell in combination with vibration, and mechanical shock are common, new third generation Pb-free alloys have been developed [9].

Sn-Zn-based alloys have received increasing attention due to their low cost and more importantly, their low melting temperature, e.g., eutectic Sn-9Zn has a melting temperature of 198 °C and shows comparable mechanical properties with Sn-37Pb [10,11]. Several studies have been carried out by both the academia and the industry, to develop a low temperature lead-free solder alloy, based on Sn-Zn or Sn-Bi solder alloys. Among them, Sn-Zn-Bi-based solder alloys are regarded as a potential “drop-in” replacement because of their relatively low melting temperature, which is similar to that of conventional Sn-37Pb [7]. Due to the great potential of Sn-Zn-Bi solder system to replace Sn-Pb as a low-temperature lead-free solder, many studies have been carried out to study the impact of micro-alloying. Ren and Collins [5] reported that the addition of Sb can significantly improve the mechanical properties of Sn-8Zn-3Bi solder alloys through microstructure refinement and solid solution strengthening. Billah et al. [12] reported that small amounts of Ni additions to Sn-8Zn-3Bi alloy refined microstructure and therefore improved mechanical properties like tensile strength and hardness. The interfacial reaction of Sn-8Zn-3Bi-xSb ($x = 0, 0.5, 1.0, 1.5$) on Cu substrate has been investigated under 150 °C thermal aging up to 720 h and an interfacial reaction mechanism, which governs the aging process, has been proposed [13]. It was found that during initial aging, CuZn_5 transformed to Cu_5Zn_8 and the intermetallic layer (IML) at the interface thickened. As aging prolonged, Cu_5Zn_8 started to degrade due to the depletion of Zn and voids formed throughout the IML. Das et al. [14] stated that the microstructure of the eutectic Sn-9Zn alloy has been affected by the addition of 0.5 wt.% Cu. They pointed out that the microstructure is composed of the β -Sn phase, α -Zn rich phase, and $\text{Cu}_6\text{Sn}_5/\text{Cu}_5\text{Zn}_8$ IMCs. The level of hardness of the ternary alloy did not change with the addition of 0.5 wt.% Cu. Rahman et al. [15] investigated the microstructure and hardness behavior of eutectic Sn-9Zn alloy reinforced with different Cu contents (0.4, 0.7, and 1.0 wt.%). They observed similar microstructures to those published by Das et al. [14]. The hardness values were found to increase with the addition of 0.4 wt.% Cu, above which the trend is reversed. The lower hardness values obtained for 0.7 and 1 wt.% Cu contents could be related to the existence of large IMCs, which consumed more α -Zn phase from the eutectic mixture resulting in a little concentration of α -Zn rich phase that presents for the eutectic reaction [16].

El-Daly and Hammad [17,18] declared that the addition of 0.7 wt.% copper to the Sn-9Zn alloy influenced its microstructural development and mechanical behavior. They confirmed the existence of the β -Sn matrix, α -Zn rich phase, and IMCs (Cu_6Sn_5 , Cu_5Zn_8 , and CuZn_5) within the microstructure of Sn-9Zn-0.7Cu alloy. They indicated that the Cu-containing alloy exhibited higher values of yield tensile strength (YTS) and ultimate tensile strength (UTS). The total elongation to failure did not change with the variation of the strain rate in both alloys examined. Lee et al. [19] studied the impact of 1, 2, and 4 wt.% copper additives on the mechanical characteristics of Sn-9Zn eutectic alloy. The values of 0.2% proof stresses and UTS of ternary alloys were close to or less than those of the Sn-9Zn eutectic alloy. As 4 wt.% copper was added to the Sn-Zn alloy, its elongation decreased from 31% to 19%. This reduction in the elongation may be attributed to the presence of a high-volume fraction of Cu-Zn IMCs in the Sn-9Zn-4Cu alloy relative to other Cu-modified alloys.

Recently, artificial neural network (ANN) model has given a fundamentally diverse approach for material modelling and material processing [20–24]. The main favorable

advantage of ANN is that it does not require hypothesis of a mathematical model at the outset or the identification of its parameters. Shakiba et al. [25] proposed an ANN model to predict the flow performance of Al-0.12Fe-0.1Si alloys with different concentrations of Cu addition (0.002–0.31 wt.%) under various deformation conditions with an average mean square error of 0.058. Mosleh et al. [26] developed an ANN model for superplastic deformation behavior of Ti-2.5Al-1.8Mn alloy at high temperatures ranging from 840 to 890 °C and in values of strain rate ranging from 2×10^{-4} to $8 \times 10^{-4} \text{ s}^{-1}$. A Mathematical model was obtained from stress–strain experimental tensile tests data. An ANN model was established to predict the flow stress as a function of temperature, strain, strain rate with root mean square error of 0.079. Abd El-Rehim et al. [27] simulated and predicted the hardness properties of Mg-9Al-1Zn alloy based on an ANN model. The results of simulation showed higher accuracy of the operating model to the experimental data. Buldum et al. [28] predicted the surface roughness during the turning process of AZ91D magnesium alloys using an artificial neural network. A good agreement was found between the predictions of the ANN model and experimental results on average surface roughness.

Several microhardness reports on the Sn-9Zn eutectic alloy have been published in the literature. Nevertheless, articles related to the impacts of aging temperature and copper content on the microstructural development and Vickers microhardness properties of newly developed low temperature lead-free solder alloys are quite limited. Since the microstructural characteristics of an alloy determine its mechanical performance, the microstructural development of a solder joint during aging process is of critical importance. To the best of authors' knowledge, no systematic study has been investigated the influence of aging temperature and Cu addition on the microstructure evolution and Vickers microhardness characteristics of Sn-9Zn alloy. The lack of such study motivated the current work. Moreover, the ANN model was adapted to derive the correlations between Vickers microhardness of Sn-9Zn alloys containing different Cu concentrations and aging temperatures. The results of the ANN were compared to the obtained experimental data.

2. Experimental Procedures

Sn-9 wt.% Zn- x Cu alloys (SZ- x Cu, with $x = 0, 1, 2, 3$, and 4 wt.%) were obtained by melting (4N Purity) granulated Sn, Zn, and Cu under a protective argon atmosphere in a muffle furnace at 673 K for 2 h. For all alloys, the zinc to tin ratio was maintained at the eutectic level for Sn-9Zn composition. The molten alloys were poured into a steel mold at 298 K (room temperature). The ingots were cut into block samples of 10 mm $\times$ 10 mm $\times$ 5 mm for Vickers microhardness tests and microstructure investigations. To verify the chemical composition of the prepared alloys, an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu, Kyoto, Japan) was utilized (Table 1). The solution heat-treatment was carried out for 24 h at 433 K in a protective argon atmosphere followed by water quenching at 298 K. The solution-treated samples were aged at several temperatures ($T_a = 323, 348, 375$, and 398 K) for 4 h then quenched in water at 298 K. The precision of the temperature measurements is within the range of ± 1 K.

Table 1. Chemical composition of the experimental Sn-9Zn- x Cu alloys analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), wt.%.

Alloy	Element Content (wt.%)		
	Zn	Cu	Sn
SZ	8.96	0	Bal.
SZ-1Cu	8.93	0.97	Bal.
SZ-2Cu	8.91	1.94	Bal.
SZ-3Cu	8.87	2.93	Bal.
SZ-4Cu	8.84	3.90	Bal.

For the microstructural characterization of the present alloys, a JSM-6480LV scanning electron microscope (JEOL JSM-6360LV Akishima, Tokyo, Japan) with energy dispersive

X-ray spectroscopy (EDS) was utilized. The SEM was operated in the secondary electron (SE) mode to evaluate surface characteristics. Phase constitutions of the present alloys were analyzed utilizing X-ray diffraction (XRD, Shimadzu D6000, Shimadzu Corporation, Tokyo, Japan, with Ni-filtered CuK α radiation ($\lambda = 1.5406 \text{ \AA}$)). The microhardness of samples was measured using a Vickers indenter (MH3, Metkon, Bursa, Turkey), with 50 g load and 10 s dwell time at 25 °C. Each recorded microhardness value was calculated using an average of 10 random indentations to ensure reproducibility.

3. Artificial Neural Network

Artificial neural network [29] is a process inspired by the human brain structure and aims to simulate brain-processing capabilities. Neurons are the main component of the neural network. Neural networks have different parts. These parts are the inputs, outputs, weight vector, and transfer function. ANN has only three layers, which are input, hidden, and output layers as shown in Figure 1. The input layer has all input factors and all parameters which depend on reaction. Information from the input layer is processed in the hidden layer. Outputs of the hidden layer(s) are also calculated in the output layer and outcome in the output vector. A feed-forward neural network is used to model this process with a back-propagation algorithm. In which the output of each neuron is only connected to the neurons of the next layer. Feed-forward neural networks usually have one or more hidden layers and have an output layer. The number of hidden layers, the number of neurons in the hidden layer, and activation function in output and hidden layers have a large effect on the performance of the network. Thus, several combinations are tried out to choose an optimal combination. To define the number of hidden layers and numbers of neurons in the hidden layer, mean square error (MSE) values obtained using Equation (1) were employed as the indices to evaluate the capability of a given network. The values of the mean square error (MSE) were used to check the performance of the used ANN [25]:

$$MSE = \frac{1}{N} \sum_{i=1}^N (E_i - P_i)^2 \quad (1)$$

where E_i is the experimental value and P_i is the predicted value obtained from the ANN. N is the total number of data employed in the study.

Figure 1. A general scheme of the three-layer network with one hidden layer.

4. Results and Discussion

Figure 2 shows the dependence of Vickers microhardness values on the Cu content for the five alloys aged at different temperatures. Worthy of notice is the fact that for all aging temperatures, the microhardness values increased with the addition of 1 and 2 wt.% Cu. In contrast, they decreased to lower values and remain almost constant in the

higher Cu-containing alloys. Moreover, from Figure 2, one can conclude that the values of microhardness decreased with increasing aging temperature for all five experimental alloys.

Figure 2. Variation of hardness with Cu content at different aging temperatures.

Figure 3a,b showing the microstructure of Sn-9Zn (SZ) eutectic alloy aged at 323 and 398 K, respectively. The microstructure is similar to those described in the literature [30,31]. The microstructure consists mainly of β -Sn and fibrous eutectic structure of β -Sn and α -Zn phases that are identified by the EDS data (Figure 3c,d). It has been reported [32,33] that the lamellar or fibrous type structures could be attributed to the rapid solidification of SZ eutectic alloy. During lamellar growth in the form of lamellae or broken- lamellae, two distinct solid phases of β -Sn and α -Zn grow cooperatively side by side. The α -Zn rich phase undergoes a fibrous growth when it grows as fibers into the β -Sn matrix. In the current work, there is an appearance of the uniform fibrous-like structure of the SZ eutectic alloy (Figure 3a,b). It should be noted that at a high aging temperature of 398 K, the microstructure of SZ alloy coarsened, and the grain size became larger which decreased the grain boundary area. Furthermore, the diffusion of Zn in the β -Sn matrix is extremely fast (10^3 times greater than self-diffusion) [34,35]. This would lead to the formation of coarsening microstructure presented in Figure 2b, resulting in lower microhardness values.

The microstructures of SZ-1Cu alloys aged at 323 and 398 K are respectively depicted in Figure 4a,b. It is clearly seen that the microstructures of ternary alloys consisting of the β -Sn phase, fibrous eutectic structure of β -Sn and α -Zn phases, rod-like (blocky) phase, and M- or H-shaped phase. The compositions of the rod-like phase and M- or H-shaped phase have been identified by the EDS analyses (Figure 4c,d).

It is interesting to note that, as can be observed in Figure 4a,b, the Cu forms two different shapes with both Sn and Zn separately. The EDX analyses revealed that the η -Cu₆Sn₅ phase has appeared as the M- or H-shaped phase while the rod-like phase is the γ -Cu₅Zn₈ phase. A magnified view presented in Figure 4b shows that the η -Cu₆Sn₅ phase develops following typical M- or H-shaped morphologies.

Figure 3. (a) SEM image of SZ alloy aged at 323 K, (b) SEM image of SZ alloy aged at 398 K, (c) EDS spectrum of Sn-Zn eutectic structure, and (d) EDS spectrum of β -Sn phase.

Figure 4. (a) SEM image of SZ-1Cu alloy aged at 323 K, (b) SEM image of SZ-1Cu alloy aged at 398 K, (c) EDS spectrum of $\gamma\text{-Cu}_5\text{Zn}_8$ phase, and (d) EDS spectrum of $\eta\text{-Cu}_6\text{Sn}_5$ phase.

Our observations agree well with those reported by El-Daly et al. [17] who detected the formation of the $\gamma\text{-Cu}_5\text{Zn}_8$ and $\eta\text{-Cu}_6\text{Sn}_5$ phases in the Sn-Zn-Cu alloys. It has been reported [36] that the Gibbs free energy of Cu-Zn IMCs formation is lower than that of Cu-Sn IMCs formation, this makes the Cu-Sn phases difficult to form. Therefore, Cu atoms will preferentially react with the active Zn to form Cu-Zn IMCs, rather than to form Cu-Sn IMCs with Sn. The diffusion speed of Cu atoms in Sn is approximately 1000–10,000 times larger than that of Zn atoms in Sn matrix [37]. Due to lower diffusivity of Zn, the supply of Zn from the solder is insufficient for CuZn_5 formation. Through aging at 323 K, the

driving formation force of the γ -phase is larger than that of the η -phase, i.e., the γ -phase is the most favorable one that will precipitate first in the matrix. Suganuma et al. [38] concluded that the Sn and Zn atoms will compete to react with Cu to form the η -Cu₆Sn₅ and γ -Cu₅Zn₈ phases respectively. The Sn atoms have a much smaller reactivity and mobility than Zn atoms, therefore the γ -Cu₅Zn₈ phase starts to form much earlier than the η -Cu₆Sn₅ phase [34].

Many researchers [39–41] have investigated the Gibbs free energy for the formation of the γ -Cu₅Zn₈ and η -Cu₆Sn₅ phases. They reported that the Gibbs free energy needed to form η -Cu₆Sn₅ phase ($\Delta G = -7.42$ kJ/mol) is greater than that of γ -Cu₅Zn₈ phase ($\Delta G = -12.34$ kJ/mol). Consequently, the γ -Cu₅Zn₈ phase will precipitate first followed by the precipitation of η -Cu₆Sn₅ phase in the solder matrix due to its smaller value of Gibbs free energy. Other researchers [42–44] reported similar results. The precipitation of fine γ -Cu₅Zn₈ and η -Cu₆Sn₅ phases in addition to the fibrous eutectic structure in the SZ-1Cu alloy can hinder localized plastic deformation during the indentation test, resulting in the notable increase in microhardness values. The low values of microhardness for aging at 398 K may be attributed to the coarsening of both γ -Cu₅Zn₈ and η -Cu₆Sn₅ IMCs of a small number and large size (Figure 4b), which are less operative to block the dislocations motion. This tendency would result in lower microhardness values.

Referring to Figure 2, it is important to perceive that the addition of 2 wt.% Cu to the SZ alloy causes an increase in microhardness values at all aging temperatures. The improvement in microhardness values could be reflected by microstructural changes detected in Figure 5.

Figure 5. (a) SEM image of SZ-2Cu alloy aged at 323 K, (b) SEM image of SZ-2Cu alloy aged at 398 K, (c) EDS spectrum of ϵ -Cu₃Sn phase.

Typical microstructures of SZ-2Cu alloys aged at 323 and 398 K are respectively presented in Figure 5a,b. It is observed that the addition of 2Cu resulted in the appearance of a new white color phase in the matrix. The EDS analysis confirmed that the white phase is the ϵ -Cu₃Sn phase. The formation of Cu₁₀Sn₃ and CuZn₅ phases is not noticeable in the current study. The formation of ϵ -Cu₃Sn, η -Cu₆Sn₅, and γ -Cu₅Zn₈ IMCs in the SZ-2Cu alloys enhanced the precipitation hardening. The formation of ϵ -Cu₃Sn IMC generates additional barriers for dislocation motion. Consequently, the dislocations initiated in the matrix cannot transfer freely, and hence, they are forced to accumulate at the interfaces, which resulted in the increased microhardness values. When the investigated samples aged at higher temperatures up to 398 K, the values of hardness are declined. This may be primarily attributed to the coarsening of the Cu₆Sn₅, Cu₅Zn₈, and Cu₃Sn precipitates. The larger precipitates grow, and smaller precipitates shrink through diffusion-controlled Ostwald ripening [45–48] (see Figure 5b). Consequently, the interaction between the moving dislocations and precipitates decreases, leading to lower microhardness values.

As can be inferred from Figure 2, a second stage distinguished by a reduction in hardness values was noticed when the Cu content exceeded 2 wt.%. Furthermore, the values of hardness are decreased by increasing the temperature of aging at any given Cu content. Tu and Thompson [49] reported that the ϵ -Cu₃Sn phase grows at the expense of η -Cu₆Sn₅ phase at a parabolic rate until the one-phase has fully vanished. Gagliano and Fine [50] detected that the ϵ -Cu₃Sn phase grew reactively at the expense of η -Cu₆Sn₅ phase after consuming all available Sn. Therefore, the larger the Cu concentration, the larger is the ϵ -phase produced. Ren and Collins [13] pointed out that as aging prolonged, γ -Cu₅Zn₈ IMC becomes unstable and begins to degrade due to the depletion of Zn and microvoids formed throughout the matrix. The development and growth of the ϵ -Cu₃Sn phase are accompanied by the formation of microvoids within the parent matrix [51]. This is manifested by the SEM images shown in Figure 6.

Figure 6. (a) SEM image of SZ-4Cu alloy aged at 323 K, (b) SEM image of SZ-4Cu alloy aged at 398 K, (c) EDS spectrum of ϵ -Cu₃Sn phase.

Figure 6a,b depict typical SEM micrographs of the SZ-4Cu alloys aged at 323 and 398 K respectively. The microstructure could be evidence of the presence of microvoids initiation (marked with red circles). The generation of microvoids may be ascribed to the unbalancing interdiffusion of Cu and Sn, which is expected to create more considerable vacancies at the interface between Cu_3Sn and Cu. The formed vacancies coalesce into microvoids [52,53]. The formation of microvoids can induce stress concentration, resulting in a decrease in hardness values. The higher the aging temperature (398 K), the higher is the total volume of microvoids, which resulting in weaken the reliability of mechanical properties of soldered joints.

Inspection of the hardness data establishes that the hardness values, H_v , are related to the aging temperature, T_a , by the following power-law equation [54,55]:

$$H_v = H_0 e^{(-\alpha T_a)} \quad (2)$$

where α is the softening coefficient and H_0 is the intrinsic hardness at 0 K [56,57]. From the above equation, the softening coefficient (α) could be evaluated from the slopes of the straight lines relating $\ln H_v$ against T_a (Figure 7). The dependence of α values on the Cu concentration is illustrated in Figure 8. From Figure 8, it is seen that the highest value of α (0.00061) is observed for the Sn-Zn eutectic alloy. This value decreased when Cu added with 1 and 2 wt.% to reach the lower value of 0.00033 for the SZ-2Cu alloy. The softening coefficient reached the values 0.00057 and 0.00059 for further addition of Cu at 3 and 4 wt.% respectively. These detected values of softening coefficient confirmed that the SZ-2Cu alloy had the highest hardness, at any given aging temperature, of all the alloys investigated. As a result of the precipitation of the $\epsilon\text{-Cu}_3\text{Sn}$, $\eta\text{-Cu}_6\text{Sn}_5$, and $\gamma\text{-Cu}_5\text{Zn}_8$ IMCs in the SZ-2Cu alloy, extra barriers for dislocation motion are existed, resulting in a lower softening coefficient of such alloy.

Figure 7. $\ln H_v$ versus aging temperature, T_a , for all the studied alloys.

Figure 8. Variation of softening coefficient, α , with Cu concentration for all the investigated alloys.

Representative XRD patterns of SZ- x Cu alloys aged 323 and 398 K are respectively shown in Figure 9a,b. All XRD charts include diffraction peaks for both β -Sn phase with the tetragonal structure according to (JCPDS card no. 04-0673) and α -Zn rich phase with the hexagonal structure at 36.8° , 43.8° , and 55.6° depending on (JCPDS card no. 01-1244). The main peaks corresponding to Cu have not been detected.

Figure 9. Representative XRD patterns of the investigated alloys aged at (a) 323 and (b) 398 K.

With the addition of Cu, one peak with a small intensity of γ -Cu₅Zn₈ IMC (JCPDS card No. 65-3157) is noticed at 43.3° owing to the interaction between copper and zinc during the solidification process of the studied alloys. Besides, it is detected the appearance of the diffraction peaks for the monoclinic η -Cu₆Sn₅ IMC. The presence of this phase in the β -Sn matrix is assured by (JCPDS card No. 45-1488). The diffraction peaks for the hexagonal ϵ -Cu₃Sn IMC (JCPDS card No. 01-1240) start to appear in the chart of SZ-2Cu alloy. The intensities of the diffraction peaks of Cu₃Sn IMC seemed to be increased for SZ-3Cu and SZ-4Cu alloys. Our results agree with those declared by Eid et al. [57,58], who deduced the existence of these three phases in the Sn-5.0Zn-0.3Cu and Sn-6.5Zn-0.3Cu alloys. From Figure 9, it can be seen that the relative diffraction peaks intensities of γ -Cu₅Zn₈ and η -Cu₆Sn₅ IMCs increased with the increment of Cu content until reaches 2 wt.% Cu and then the intensities decreased for the alloys containing 3 and 4 wt.% Cu. This explains the elevation in the hardness values for SZ-1Cu and SZ-2Cu alloys. The reduction in the hardness values for SZ-3Cu and SZ-4Cu alloys may be rendered to the formation and growth of ϵ -Cu₃Sn phase that is accompanied by the formation of microvoids in the solder matrix.

According to Scherrer's equation [59], the average crystallite size, D , of the β -Sn matrix could be evaluated using the formula given below:

$$D = 0.9\lambda / (\beta \cos \theta) \quad (3)$$

where λ is the X-ray wavelength, θ is the X-ray diffraction's angle, and β is the full width of the diffraction peak at its half maximum intensity. The dependence of the average crystallite size, D , on the Cu content at different T_a values is depicted in Figure 10a. The D values decline with increasing Cu content from 0 to 2 wt.%, thereafter further Cu concentration (3 and 4 wt.%) led to an increase of the D values. Moreover, the elevation of D values is observed with the variation of aging temperatures from 323 to 398 K. As the Cu weight percentage increases up to 2 wt.%, the grains were refined which produces more grain boundaries and improves the hardness of such alloys. In order to evaluate both the dislocation density, δ , and the lattice strain, ϵ , the following equations were applied [60,61]:

$$\delta = \frac{1}{D^2} \quad (4)$$

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (5)$$

Figure 10b,c represent the variation of both δ and ϵ for the investigated β -Sn phase with the Cu content at different aging temperatures. The results demonstrate that a reverse relationship exists between both the dislocation density and lattice strain with the average crystallite size. Due to the refinement of the crystallite size with increasing the Cu weight percentage up to 2 wt.% Cu, an effective number of the dislocation density and grain boundaries is generated. Consequently, high lattice strain is produced which improves the hardness and the mechanical performance of the alloys.

Furthermore, the stacking fault probability, SFP , of SZ- x Cu alloys at various aging temperatures was evaluated by utilizing the following equation [62]:

$$SFP = \frac{2\pi^2 \Delta(2\theta)}{45\sqrt{3} \tan \theta_{200}} \quad (6)$$

where $\Delta(2\theta)$ is the diffraction peak shift for the (200) plane. The diffraction peak position is shifted due to the increment in the stacking fault [62]. Figure 10d shows the variation of SFP with Cu content at different aging temperatures. The maximum value of SFP was reached at 2 wt.% Cu, at all aging temperatures, which means the improvement of the hardness of SZ-2Cu alloy.

Figure 10. The Cu content dependence of (a) average crystallite size, D , (b) dislocation density, δ , (c) lattice strain, ε , and (d) stacking fault probability, SFP , of the investigated alloys at different aging temperatures.

Neural systems were trained and predicted simultaneously using experimental data of Vickers microhardness at various Cu concentrations (0, 1, 2, 3, and 4 wt.%) and aging temperatures (323, 348, 373, and 398 K). The experimental data is partitioned into two sets; training set and prediction set. The training set is utilized to train the ANN. The prediction data set is used to confirm the accuracy of the ANN model. ANN was used to training hardness at temperatures (323, 348, and 373 K) and prediction at temperature 398 K. A proposal block diagram of Sn-9Zn binary eutectic alloy using ANN is given as two inputs and one output as shown in Figure 11. The inputs are Cu concentration (0, 1, 2, 3, and 4 wt.%) at different aging temperatures (323, 348, and 373 K). The output is the microhardness. With this information, numerous network designs were created to improve the mean square error (MSE) and obtain great network performance. ANN having three hidden layers of 17, 15, and 19 neurons. The output was chosen to be a pure line, while the transfer functions of these hidden layers were chosen to be logsig. The procedures for training are presented in Figure 12. The best MSE for each network was 9.5731×10^{-6} after 131 training epochs. Appendix A shows the obtained equation representing the hardness profile. Results of simulation, prediction, and experimental values are shown in Figure 13. Hardness simulated at temperatures of 323, 348 and 373 K, and predicted at the temperature of 398 K. Figure 13 demonstrates that the simulated result and the experimental data of hardness are in good agreement, which indicates that networks training takes on optimal generalization performance. The performance of the ANN model was validated by comparing the prediction values at temperature 398 K with the measured experimental data. The predicted values were in good agreement with the measured dataset. In summary, the results indicated higher precision of the ANN model to the experimental data.

Figure 11. A proposal block diagram of Sn-Zn-Cu alloys using ANN.

Figure 12. Evolution of training and test errors as a function of the number of training (epochs) of Sn-Zn-Cu alloys using ANN model.

Figure 13. Simulation and prediction of the hardness-profile of Sn-Zn-Cu alloys based-ANN model.

5. Conclusions

Based on the investigations described above, the following conclusions were derived:

- (1) The hardness values of the investigated alloys increased with the Cu content up to 2 wt.%, above which the behavior is changed oppositely.
- (2) The microstructure of Sn–9Zn binary eutectic alloy can be modified through copper addition.
- (3) The hardness values decreased as the aging temperature increased at any given concentration of Cu.
- (4) The alteration of the hardness values with Cu content and/or aging temperature was interpreted based on the formation, growth, and dissolution of formed phases.

- (5) The behavior of the average crystallite size, dislocation density, lattice strain, and stacking fault probability, calculated from the XRD profiles, is compatible with the trend of hardness behavior.
- (6) Based on the ANN model, simulation and prediction of Sn–9Zn–Cu alloys showed a high correspondence with extremely low mean square error (MSE). The results showed higher precision of the ANN model to the experimental data.
- (7) Mathematical equation described experimental data was obtained using the ANN.

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Appendix A

The equation which describes hardness is given by:

$$H = \text{pure line} [\text{logsig net.LW}\{4, 3\} \text{logsig} (\text{net.LW}\{3, 2\} \text{logsig} (\text{net.LW}\{2, 1\} \text{logsig} (\text{net.IW}\{1, 1\}T + \text{net.b}\{1\}) + \text{net.b}\{2\}) + \text{net.b}\{3\}) + \text{net.b}\{4\}]$$

where T is the inputs (temperatures and concentration of Cu), net.IW{1, 1} is linked weights between the input layer and first hidden layer, net.LW{2, 1} is linked weights between first and second hidden layer, net.LW{3, 2} is linked weights between the second and third hidden layer, net.LW{4, 3} is linked weights between the third and output layer, net.b{1} is the bias of the first hidden layer, net.b{2} is the bias of the second hidden layer, net.b{3} is the bias of the third hidden layer, and net.b{4} is the bias of the output layer.

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