

# Microstructural evolution and mechanical properties of Sn-Bi-Cu ternary eutectic alloy produced by directional solidification

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Sn-36Bi-22Cu (wt.%) ternary eutectic alloy was prepared using vacuum melting furnace and casting furnace. The samples were directionally solidified upwards solidification rate varying from 8.3 to 166  $\mu\text{m/s}$  and at a constant temperature gradient (4.2 K/mm) in a Bridgman-type directional solidification furnace. The composition analysis of the phases and the intermetallics ( $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$ ) were determined from EDX and XRD analysis respectively. The variation of the lamellar spacing (Bi-rich phase) and the  $\text{Cu}_3\text{Sn}$  phase spacing with the solidification rate were investigated. The dependence of microhardness, ultimate compressive strength and compressive yield strength on solidification rate were determined. The spacing and microhardness were measured from both longitudinal and transverse sections of the samples. The dependence of microhardness on the lamellar spacing and the  $\text{Cu}_3\text{Sn}$  phase spacing were also determined. The relationships between phase spacings, solidification rate and mechanical properties were determined from linear regression analysis.

**Keywords:** Directional solidification, eutectic alloy, microstructure, intermetallic compound, microhardness, compressive strength.

## 1. Introduction

Solidification plays a vital role since it forms the basis for influencing the microstructure and hence improving the quality of cast products. For this improving the casting production and solidification methods have a significant effect on the mechanical properties of the materials and enhancing the quality of cast metals<sup>1-4</sup>. Directional solidification<sup>5</sup> is one of the most important solidification methods used for material processing. The mechanical properties of the alloys can be improved by obtaining finer microstructure result from higher solidification rates and higher cooling rates under several directional solidification conditions<sup>6-13</sup>. The directionally solidified alloy exhibited higher strength than the non-directionally solidified alloy under the same cooling rate<sup>14,15</sup>. Liu et al.<sup>16</sup> reported that the tensile strength of the in situ composite from the directionally solidified alloy is significantly higher than that from the as-cast alloy.

Soldering technology is an essential part of electronic devices since it plays a key role not only as an electrical connection but also as a mechanical bond<sup>17,18</sup>. Currently, solder joints with higher reliability is demanding because the trend in electronic package is to make products smaller and faster. For global environment conservation, many researches

on replacing the conventional Pb-Sn eutectic solder with a lead-free solder have been carried out. Among various lead-free solders, Sn-Bi alloy is one of the promising candidates<sup>19</sup>. Furthermore, the ternary Sn-Bi-Cu ternary alloys may also be considered as promising lead-free solders<sup>19</sup>. Recently, Ag, Bi or In-containing Sn-Cu alloys have received some attention, and in several prominent reliability test programs Sn-Cu-Ag and Sn-Cu-In alloys demonstrated superior performance, at least in its mechanical strength<sup>20,21</sup>. Tai et al.<sup>22</sup> showed that creep resistance of Sn-3.5Ag was improved significantly for Cu particle-reinforced composite solder joints at 25 °C, 65 °C and 105 °C. The tensile strength increased with increasing Bi content in the Sn-Cu eutectic solder alloy, which was attributed to the presence of Bi and its role in refining microstructure and solid solution strengthening<sup>23</sup>. Zhang et al.<sup>24</sup> reported that Sn-Bi-Cu alloys were found to have greater wettability than the Sn-Ag-Cu alloy, and it was confirmed that the addition of Bi increases the wettability. The effect of  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  intermetallics (IMC's) on the mechanical properties were investigated from many researchers<sup>25,26</sup>. Cheng et al.<sup>25</sup> reported that,  $\text{Cu}_3\text{Sn}$  single crystal consist of high ultimate strengths depending on the material directions and strain rate. Hu et al.<sup>26</sup> reported that,

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increased amount of  $\text{Cu}_3\text{Sn}_5$  fibers caused an increment in both ultimate tensile strength and yield tensile strength. The mechanical properties (microhardness, shear stress, young and bulk modulus) and the wettability of the SnCu solder were improved with Bi addition<sup>27</sup>. There are numerous works on low solute content (Cu) Sn-based alloys<sup>8,23-31</sup>. Nevertheless, there has been only a limited amount of data about the mechanical properties of directionally solidified high solute content (Cu) Sn-based alloy. In this study, Sn-Bi-Cu ternary alloy containing high Cu is preferred. Similar alloys are used as soldering or brazing material depending on the content of copper. The aim of the present work is to investigate the effect of solidification rate ( $V$ ) on microstructure ( $\lambda$ ), microhardness (HV) and compressive strength ( $\sigma$ ) of the directionally solidified Sn-36Bi-22Cu (wt.%) ternary eutectic alloy. The dependence of microhardness on the lamellar spacing (Bi-rich phase) and the  $\text{Cu}_3\text{Sn}$  IMC phase spacing were also determined.

## 2. Experimental Procedure

### 2.1. Alloy preparation, directional solidification and metallographic processes

Weighed quantities of Sn, Bi and Cu metals in a graphite crucible determined from stoichiometric calculations were placed in a vacuum melting furnace, and the metals were completely melted. After allowing time for the melt to become homogeneous, the molten alloy was poured into graphite crucibles in a casting furnace. The molten alloy solidified from bottom to top in the casting furnace. The directional solidification of the produced alloy was performed in a Bridgman-type directional solidification furnace whose schematic diagram is given in Figure 1. For the directional solidification, the sample was placed into the sample holder. The sample was placed into the furnace. After the furnace reached the desired temperature and thermal stabilization, the sample was withdrawn from the hot region to the cold region of the furnace with the help of different speeded synchronous motors. The alloy was directionally solidified under different solidification rates (8.3-166  $\mu\text{m/s}$ ) at a constant temperature gradient (4.2 K/mm). When the sample solidified 12-13 cm, it was quenched in water. Details of the furnaces equipment, alloy preparation, and directional solidification are given in previous work<sup>32</sup>.

For the metallographic processes, the longitudinal and the transverse sections of the samples were cold mounted with epoxy-resin. The samples were then ground with 320-4000 grit SiC paper and polished with 3-0.25  $\mu\text{m}$  diamond pastes. The alloys were then etched with 95 ml  $\text{H}_2\text{O}$ , 2.5 ml  $\text{HNO}_3$ , 1.5 ml HCl, 1 ml HF. The micrographs of the samples were taken with the Olympus BX-51 model optical microscope by using different objectives. The lamellar spacing,  $\lambda$  (Bi-rich

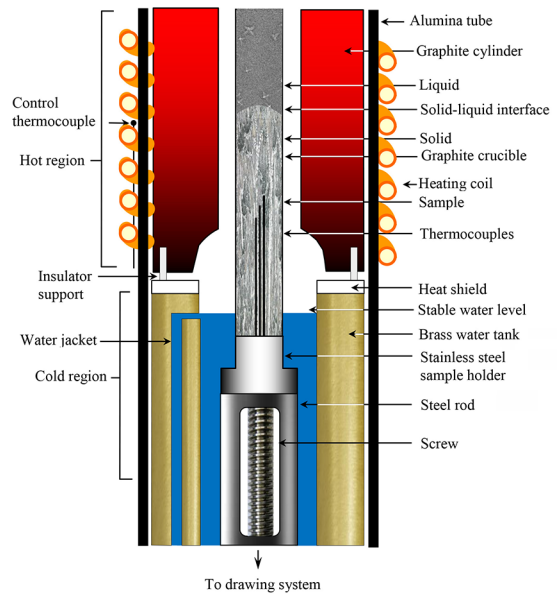


Figure 1. The Bridgman-type directional solidification furnace

phase) and the  $\text{Cu}_3\text{Sn}$  intermetallic phase spacings ( $\lambda_i$ ) were measured with the Adobe Photoshop CS3 program taking into account the magnification factor. In eutectic and intermetallic phase spacing measurements, linear intersection method is used. In both measurements, at least 30-50 values were measured for each specimen at least on ten different regions for each specimen for statistical reliability. The details of eutectic and particle spacing measurements were described elsewhere<sup>32</sup>.

### 2.2. Measurement of microhardness

Microhardness measurements were performed with a Future Tech FM-700 model digital microhardness test device. This device has the ability of applying 1-1000 g load. In this work 10 g load was applied to the sample for 10 seconds. The measurements were taken from the solid parts nearest to the solid-liquid interface. Average of 30 measurements were taken from longitudinal and transverse sections of the directionally solidified samples, and the average values were taken for the microhardness value. When the indenter of the test device applied to the sample for certain times, the trace in the shape of square occurs. The diagonal size of the trace ( $d$ ) is read from the test device. By dividing the applied force by the trace area the Vickers microhardness is determined as follows

$$HV = \frac{2P \sin(\theta/2)}{d^2} \quad (1)$$

where  $P$  is the applied load (kg),  $d$  is the diagonal length of trace,  $\theta$  is the angle between the opposite surfaces of the diagonal trace.

### 2.3. Measurement of compressive strengths

The dependence of ultimate compressive strength and compressive yield strength on the solidification rate were determined. In this work, round rod samples have a length of 6-8 mm and a diameter of 4 mm were used. Compressive strength measurements of the samples were made at room temperature at a deformation rate of 1 mm/min. Compressive tests were performed to the directionally solidified round rod samples with different solidification rates.

## 3. Results and Discussion

### 3.1 Determination of the chemical components of the phases

According to the binary phase diagrams among Bi, Sn and Cu, solid solubility of Sn in solid Bi and Bi in solid Sn are about 0.1 wt.% Sn and 21 wt.% Bi, respectively at the eutectic temperature, 139°C<sup>33</sup>. Also, the solubility of solid Sn in Cu and solid Cu in Sn are about 1 wt.% and 0.006 wt.%, respectively at the eutectic temperature, 232°C<sup>33</sup>. Previous work<sup>34</sup> indicated that the calculated solubilities of Bi in solid Cu or Cu in solid Bi at the eutectic point are both approximately 10<sup>-9</sup> with the assumption that the interchange energy in the rhombohedral structure is similar to that in the fcc structure. This small amount cannot be detected with modern spectroscopy, and the material is normally treated as a pure material<sup>34</sup>.

Energy dispersive X-ray (EDX) analysis was performed to determine the composition of phases in the Sn-Bi-Cu eutectic alloy. EDX analysis was performed at 20 keV using the X-ray lines. According to the EDX analysis results shown in Figure 2, four different solid phases (black, dark gray, white lamellar and dark lamellar) grew at the Sn-Bi-Cu eutectic alloy. The compositions of the black phase (Cu<sub>3</sub>Sn intermetallic) and dark gray phase (Cu<sub>6</sub>Sn<sub>5</sub> intermetallic) were Cu-wt.% 40.70 Sn and Sn-wt.% 35.75 Cu, respectively. Also, the white lamellar phase (Bi-rich eutectic) and dark lamellar phase (Sn-rich eutectic) were Bi-3.38 wt.% Sn and Bi-24.16 wt.% Sn, respectively. Figure 2 shows examples of representative SEM images of ternary eutectic microstructures obtained for the directionally solidified Sn-36Bi-22Cu alloys, with the eutectic mixtures being characterized by complex arrangements of Bi-rich and Sn-rich phases and the corresponding intermetallic compounds, Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub>, respectively. For the Cu<sub>3</sub>Sn IMC, its growth is governed by the reaction between Cu and Sn atoms. Clevenger et al.<sup>35</sup> reported the onset of Cu<sub>3</sub>Sn formation from the reaction between Cu<sub>6</sub>Sn<sub>5</sub> and Cu. The Cu<sub>3</sub>Sn phase can be formed by conventional casting<sup>36,37</sup>, directional solidification<sup>8,23,26</sup> and rapid solidification methods<sup>38-40</sup>. Due to the solidification temperature differences, initially the Cu-rich Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> IMC phases solidified, followed by Sn-rich and

Bi-rich phases at a lower temperature. Ternary cooperative growth has not been observed for this reason. In addition, the presence of these phases was confirmed by EDX (Fig.2) and XRD analysis (Fig.3). According to Fig.2, Cu<sub>3</sub>Sn particles with a thickness about 4 μm were surrounded by Cu<sub>6</sub>Sn<sub>5</sub> phase and these two phases are coherent with each other very well. During the eutectic reaction, the Cu<sub>3</sub>Sn IMC phase grows as rods embedded in a continuous Bi-rich matrix.

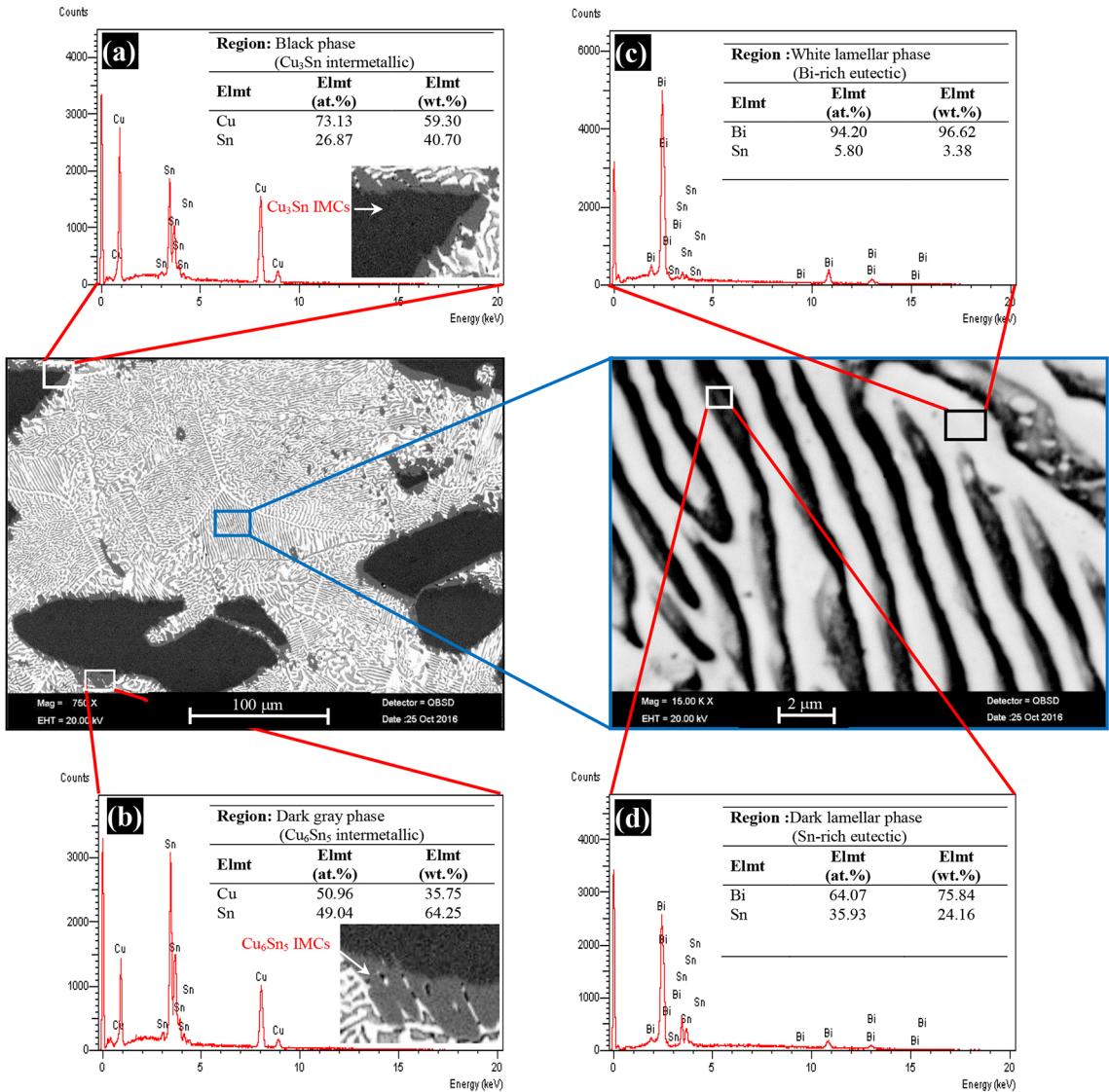
X-ray diffraction (XRD) measurements were performed with a diffractometer (Rigaku Ultima IV) using Cu-Kα radiation (k=1.5405 Å) at an accelerating voltage of 40 kV. The diffracted beam was scanned in steps by 0.01° across a 2θ range of 10-100°. XRD results of as-cast alloy are shown in Figure 3. As indicated, the presence of Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> is confirmed due to the high number of peaks corresponding to these phases. Bi was not observed present in the Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> IMC phases, and Bi did not form IMCs in the interfacial reactions. The Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> intermetallics have rod-like morphologies, being characterized as faceted phases. Cu<sub>3</sub>Sn IMC is a more stable phase than Cu<sub>6</sub>Sn<sub>5</sub> IMC. The Cu<sub>3</sub>Sn intermetallic particles may grow in a rod-like form without branches, as shown in Figure 4. Kim et al.<sup>41</sup> reported similar morphologies for the Cu<sub>6</sub>Sn<sub>5</sub> and Ag<sub>3</sub>Sn particles in Sn-Ag-Cu alloys.

### 3. 2 Effect of solidification rate on microstructure

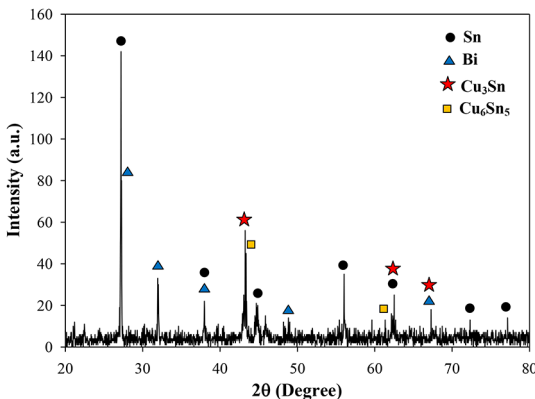
The optic micrographs of the longitudinal and transverse sections of directionally solidified Sn-Bi-Cu eutectic alloy at different solidification parameters are shown in Figure 4. The microstructure is formed by dispersed rod-like particles of Cu<sub>3</sub>Sn within Sn-rich and Bi-rich phases. Cu<sub>3</sub>Sn IMC appears for each solidification rate. Cooling condition has a significant effect on the IMC thickness. For a constant temperature gradient (4.2 K/mm), it is found that the complex regular Bi-Sn lamellar spacings and Cu<sub>3</sub>Sn intermetallic phase spacings are mainly controlled by the solidification rate (V), and both of them decrease with increased solidification rate. Spacings between primary intermetallic particles (Cu<sub>3</sub>Sn) were measured. These particles are part of the complex regular eutectic microstructure. At the highest growth rate (166 μm/s), the average spacing between the particles is reduced to 22 μm. Consequently, the microstructure underwent are finement with an increase in the solidification rate (Table 1).

Higher solidification rate yields a thinner IMC, which is consistent with other researchers' results<sup>42,43</sup>. Because of its mechanical properties, Cu<sub>3</sub>Sn is also more suitable than Cu<sub>6</sub>Sn<sub>5</sub> and Sn as a joint material for microbumps<sup>44,45</sup>.

Rod-like Cu<sub>3</sub>Sn particles prevailed along the Bi-rich eutectic matrix, as can be seen in Fig. 4. These hard and brittle Cu<sub>3</sub>Sn particles are normally alternated with the Bi-rich phase permitting the eutectic mixture to be characterized. According to Figure 4, The primary Cu<sub>3</sub>Sn intermetallic phases with a thickness about 4 μm were surrounded by Cu<sub>6</sub>Sn<sub>5</sub> intermetallic phases for lowest solidification rate (8.3 μm/s) and these two



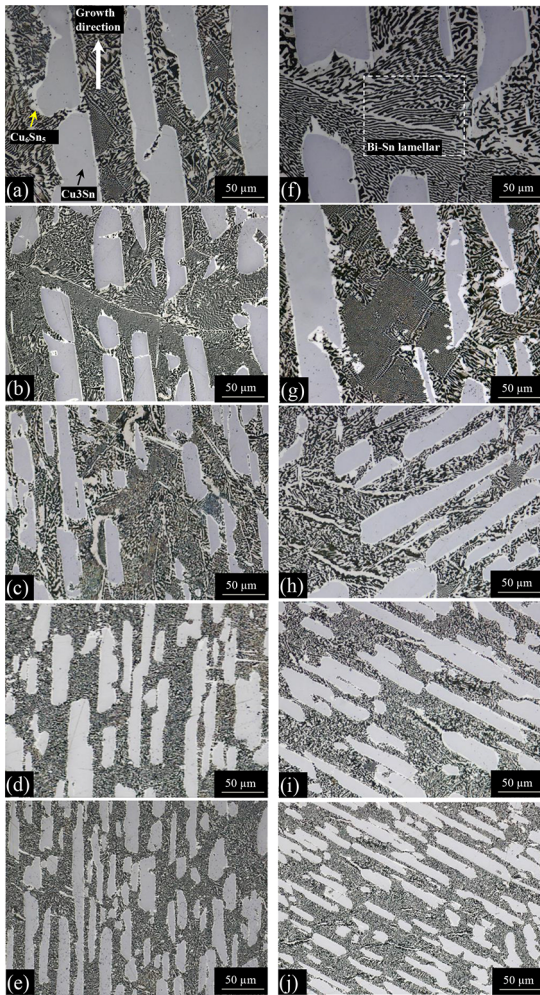
**Figure 2.** The chemical composition analysis of Sn-36Bi-22Cu eutectic alloy ( $G=4.2$  K/mm,  $V=8.3$   $\mu\text{m/s}$ ) by using SEM-EDX, (a) black phase ( $\text{Cu}_3\text{Sn}$  intermetallic phase) (b) dark gray phase ( $\text{Cu}_6\text{Sn}_5$  intermetallic phase) (c) white lamellar phase (Bi-rich eutectic phase) (d) dark lamellar phase (Sn-rich eutectic phase)



**Figure 3.** X-ray diffraction patterns obtained from the Sn-36Bi-22Cu alloy

phases are coherent with each other very well. With increasing the solidification rate from 8.3 to 166  $\mu\text{m/s}$ , the thickness of  $\text{Cu}_6\text{Sn}_5$  intermetallic phase decreased from 4.15  $\mu\text{m}$  to 0.75  $\mu\text{m}$ . The thickness of the  $\text{Cu}_6\text{Sn}_5$  phase agrees with the thickness found by Chen<sup>46</sup>, Le et al.<sup>47</sup> and Rao et al.<sup>48</sup>. The variation of lamellar spacing ( $\lambda$ ) and  $\text{Cu}_3\text{Sn}$  intermetallic phase spacing ( $\lambda_1$ ) with solidification rate are given in Table 1 and Figure 5, and the relationships between these parameters are given in Table 2. At a constant temperature gradient (4.2 K/mm), the  $\lambda$  and  $\lambda_1$  decreased with increasing solidification rate. The average eutectic spacing values measured on the longitudinal ( $\lambda_L$ ) and transverse ( $\lambda_T$ ) sections of the samples are given in Table 1. With increasing the solidification rate from 8.3 to 166  $\mu\text{m/s}$ ,  $\lambda_L$  (lamellar) decreased from 2.72 to





**Figure 4.** Optical images of the directionally solidified Sn-36Bi-22Cu eutectic alloy at a constant temperature gradient ( $G=4.2$  K/mm) (a-e) longitudinal section ( $V=8.3$ - $166.0$   $\mu\text{m/s}$ ), (f-j) transverse section ( $V=8.3$ - $166.0$   $\mu\text{m/s}$ )

$1.41$   $\mu\text{m}$ ,  $\lambda_T$  (lamellar) decreased from  $2.89$  to  $1.50$   $\mu\text{m}$ ,  $\lambda_{TL}$  (for  $\text{Cu}_3\text{Sn}$  phase) decreased from  $98.3$  to  $18.6$   $\mu\text{m}$  and  $\lambda_{TT}$  (for  $\text{Cu}_3\text{Sn}$  phase) decreased from  $108.0$  to  $25.4$   $\mu\text{m}$ . The exponent value ( $0.24$ - $0.25$ ) of the  $V$  is in good agreement with the values of  $0.22$ - $0.26$ ,  $0.25$  obtained by Şahin and Çadırılı<sup>49</sup> for Bi-2.0Zn-0.2Al (wt.%) eutectic alloy, by Yan et al.<sup>50</sup> for Nb-22Ti-16Si-3Cr-3Al-2Hf (at.%) alloy, respectively. Since ternary cooperative growth has not been observed in this study, the exponent value of  $0.5$  predicted by the Jackson-Hunt eutectic theory<sup>51</sup> for binary eutectics was not obtained. However, as can be seen from Table 2, an exponent value of  $0.52$  was obtained for the dependence of the  $\text{Cu}_3\text{Sn}$  phase spacings related to solidification rate.

### 3.3. Effect of solidification rate on microhardness

The dependence of microhardness on the solidification rate and phase spacing is given in Table 1 and Figures 6 and 7, and the relationships between these parameters are given in Table 3. At a constant temperature gradient ( $4.2$  K/mm), the microhardness values increased with increasing solidification rate. The average microhardness values measured on the longitudinal and transverse sections of the samples are given in Table 1. With increasing the solidification rate from  $8.3$  to  $166$   $\mu\text{m/s}$ , the  $\text{HV}_L$  increased from  $192.7$  to  $290.8$  MPa and  $\text{HV}_T$  increased from  $193.2$  to  $296.7$  MPa. Also, the  $\text{HV}_{LL}$  ( $\text{Cu}_3\text{Sn}$  phase) increased from  $3054.8$  to  $3436.4$  MPa and  $\text{HV}_{TT}$  ( $\text{Cu}_3\text{Sn}$  phase) increased from  $2663.4$  to  $3144.1$  MPa. The measured microhardness values for the  $\text{Cu}_3\text{Sn}$  phase are in good agreement with the values of  $3364.8$ ,  $3266.7$ - $2795.9$  ( $0.98$ - $4.9$  N load),  $3364.8$  and lower than the  $4231.1$ - $4184.9$  MPa ( $1.96$ - $4.9$  N load) obtained by Lee et al.<sup>52</sup>, Liu et al.<sup>53</sup>, Frear et al.<sup>54</sup> and Ghosh<sup>55</sup>, respectively.

The exponent value ( $0.13$ - $0.14$ ) of the  $V$  (for lamellar structure) is in good agreement with the value of  $0.14$ ,  $0.11$ ,  $0.15$ , values obtained by Zhang et al.<sup>7</sup> for Ni-25at.%Si alloy, by Hu et al.<sup>56</sup> for Sn-1.0 wt.% Cu, by Fan et al.<sup>57</sup> for Ti-46Al-0.5W-0.5Si alloy (at.%), respectively. Decrease in lamellar spacing due to the increasing solidification rate, increased the microhardness. As can be seen from Table 1 and Figure 7, microhardness increased with decreasing lamellar spacing. With decreasing the  $\lambda_L$  from  $2.72$  to  $1.41$   $\mu\text{m}$ ,  $\text{HV}_L$  increased from  $192.7$  to  $290.8$  MPa. With decreasing the  $\lambda_{LL}$  from  $98.3$  to  $18.6$   $\mu\text{m}$ ,  $\text{HV}_{LL}$  increased from  $3054.8$  to  $3436.4$  MPa. Similarly, With decreasing the  $\lambda_T$  from  $2.89$  to  $1.50$   $\mu\text{m}$ ,  $\text{HV}_T$  increased from  $193.2$  to  $296.7$  MPa. With decreasing the  $\lambda_{TT}$  from  $108.0$  to  $25.4$   $\mu\text{m}$ ,  $\text{HV}_{TT}$  increased from  $2663.4$  to  $3144.1$  MPa.

The increment of the solidification rate not only decrease the  $\text{Cu}_3\text{Sn}$  IMC spacings but also refines the  $\text{Cu}_3\text{Sn}$  IMC phases. The finer microstructure causes an increment on the mechanical properties. The microhardness values of the  $\text{Cu}_3\text{Sn}$  phases are approximately  $10$ - $15$  times greater than the complex Bi-Sn eutectic phase. However, the change in complex lamellar spacing is more effective on microhardness. As shown in Table 3, the exponent value ( $0.53$ ) of the Bi-Sn complex lamellar phase is quite larger than the exponent value ( $0.09$ ) of the  $\text{Cu}_3\text{Sn}$  IMC phase. This is due to the fact that the dependency of the Bi-Sn complex lamellar spacing on the solidification rate is quite large relative to the  $\text{Cu}_3\text{Sn}$  IMC phase spacing. The exponent value ( $0.53$ ) of the lamellar phase is good agreement with the  $0.50$  value obtained by Spinelli et al.<sup>30</sup> for Sn-Cu solder alloys

**Table 1.** Experimental data of the Sn-36Bi-22Cu alloy.

G (K/mm)	V ( $\mu\text{m/s}$ )	$\lambda$ ( $\mu\text{m}$ )	$\lambda_1$ ( $\mu\text{m}$ )	HV (MPa)	Thickness of $\text{Cu}_3\text{Sn}_5$ ( $\mu\text{m}$ )	$\text{HV}_1$ (MPa)	$\sigma_y$ (MPa)	$\sigma_c$ (MPa)
4.2	8.3	2.81	103.1	192.9	4.15	2859.1	71.5	102.1
4.2	16.6	2.60	73.2	215.1	3.29	2958.2	91.0	110.0
4.2	41.5	1.78	37.2	233.6	2.10	3042.1	103.3	113.0
4.2	83.0	1.51	30.4	260.0	1.68	3124.5	112.3	116.3
4.2	166.0	1.46	22.0	293.7	0.75	3290.3	118.9	139.3

$\lambda$ : the value of the lamellar spacing

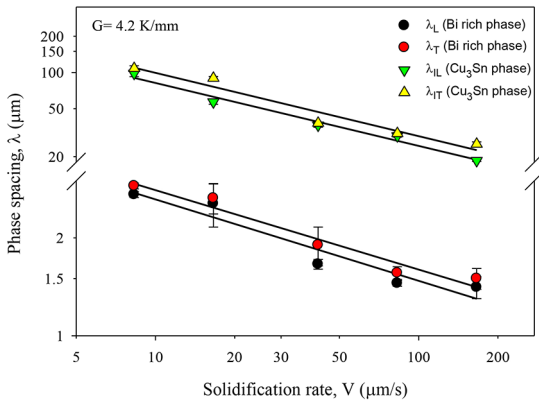
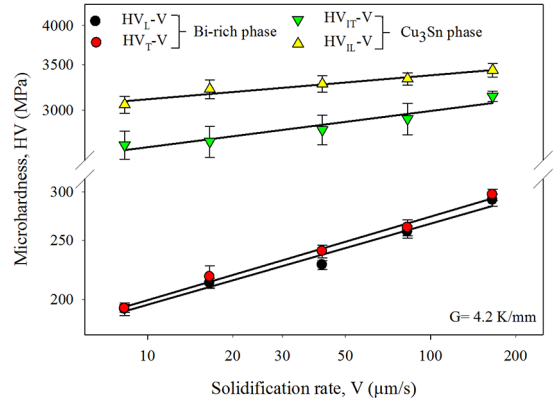
$\lambda_1$ : the value of the  $\text{Cu}_3\text{Sn}$  intermetallic phase spacing

HV: the microhardness value of the lamellar structure

$\text{HV}_1$ : the microhardness value of the  $\text{Cu}_3\text{Sn}$  intermetallic phase

$\sigma_y$ : the value of the compressive yield strength

$\sigma_c$ : the value of the ultimate compressive strength.

**Figure 5.** Variation of phase spacings versus solidification rate**Figure 6.** Variation of microhardness versus solidification rate**Table 2.** The relationships between the microstructure parameters and the solidification rate

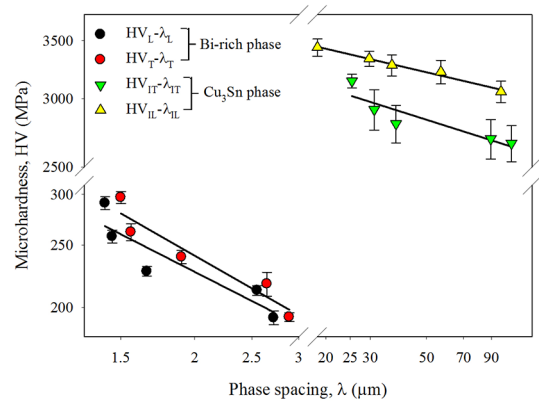
Relationships	Constant (k)	Correlation Coefficient (r)
$\lambda_{IL} = k_1 V^{0.52}$	$k_1 = 273.53$ ( $\mu\text{m}^{1.52} \text{s}^{-0.52}$ )	$r_1 = -0.990$
$\lambda_{IT} = k_2 V^{0.53}$	$k_2 = 333.43$ ( $\mu\text{m}^{1.53} \text{s}^{-0.53}$ )	$r_2 = -0.973$
$\lambda_L = k_3 V^{0.25}$	$k_3 = 4.68$ ( $\mu\text{m}^{1.25} \text{s}^{-0.25}$ )	$r_3 = -0.960$
$\lambda_T = k_4 V^{0.24}$	$k_4 = 4.92$ ( $\mu\text{m}^{1.24} \text{s}^{-0.24}$ )	$r_4 = -0.979$

$\lambda_{IL}$ : the spacings between the  $\text{Cu}_3\text{Sn}$  intermetallic phases measured from the longitudinal section of the sample

$\lambda_{IT}$ : the spacings between the  $\text{Cu}_3\text{Sn}$  intermetallic phases measured from the transverse section of the sample

$\lambda_L$ : the values of the lamellar spacing (Bi rich phase) measured from the longitudinal section of the sample

$\lambda_T$ : the values of the lamellar spacing (Bi rich phase) measured from the transverse section of the sample.

**Figure 7.** Variation of microhardness versus phase spacing

**Table 3.** The relationships between the solidification rate and the mechanical properties

Relationships	Constant (k)	Correlation Coefficient (r)
$HV_L = k_1 V^{0.13}$	$k_1 = 360.83 \text{ (MPa mm}^{-0.13} \text{s}^{0.13})$	$r_1 = 0.989$
$HV_T = k_2 V^{0.14}$	$k_2 = 374.11 \text{ (MPa mm}^{-0.14} \text{s}^{0.14})$	$r_2 = 0.996$
$HV_{IL} = k_3 V^{0.04}$	$k_3 = 3660.16 \text{ (MPa mm}^{-0.04} \text{s}^{0.04})$	$r_3 = 0.971$
$HV_{IT} = k_4 V^{0.05}$	$k_4 = 3379.87 \text{ (MPa mm}^{-0.05} \text{s}^{0.05})$	$r_4 = 0.959$
$HV_L = k_5 \lambda^{-0.47}$	$k_5 = 12.31 \text{ (MPa mm}^{0.47})$	$r_5 = -0.913$
$HV_T = k_6 \lambda^{-0.53}$	$k_6 = 9.15 \text{ (MPa mm}^{0.53})$	$r_6 = -0.956$
$HV_{IL} = k_7 \lambda^{-0.07}$	$k_7 = 2622.41 \text{ (MPa mm}^{0.07})$	$r_7 = -0.991$
$HV_{IT} = k_8 \lambda^{-0.09}$	$k_8 = 2145.85 \text{ (MPa mm}^{0.09})$	$r_8 = -0.902$
$\sigma_c = k_9 V^{0.09}$	$k_9 = 153.74 \text{ (MPa mm}^{-0.09} \text{s}^{0.09})$	$r_9 = 0.914$
$\sigma_y = k_{10} V^{0.16}$	$k_{10} = 165.99 \text{ (MPa mm}^{-0.16} \text{s}^{0.16})$	$r_{10} = 0.962$

$HV_L$ : the value of the microhardness measured from the longitudinal section of the lamellar structure

$HV_T$ : the value of the microhardness measured from the transverse section of the lamellar structure

$HV_{IL}$ : the value of the microhardness measured from the longitudinal section of the  $\text{Cu}_3\text{Sn}$  intermetallic phase

$HV_{IT}$ : the value of the microhardness measured from the transverse section of the  $\text{Cu}_3\text{Sn}$  intermetallic phase

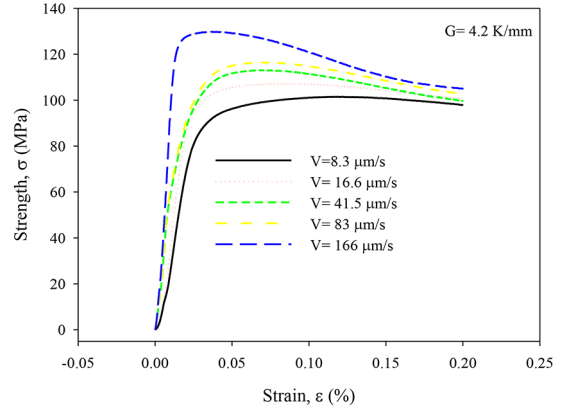
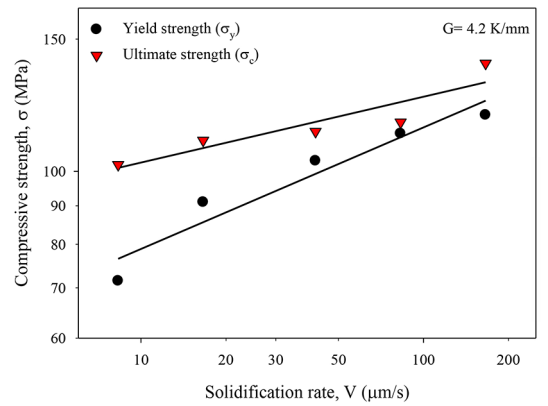
$\sigma_c$ : the values of the ultimate compressive strength

$\sigma_y$ : the values of the compressive yield strength

### 3.4 Effect of solidification rate on compressive strength

Compressive strength-strain curves for Sn-36Bi-22Cu alloy are shown in Figure 8. The variation of ultimate compressive strength ( $\sigma_c$ ) and compressive yield strength ( $\sigma_y$ ) determined from strength-strain curves with solidification rate are given in Figure 9 and Table 1, and the relationships between these parameters are given in Table 3. At a constant temperature gradient (4.2 K/mm), the compressive strength values increased with increasing solidification rate. With increasing the solidification rate from 8.3 to 166  $\mu\text{m/s}$ , the  $\sigma_c$  increased from 102.1 to 139.3 MPa and the  $\sigma_y$  increased from 71.5 to 118.9 MPa. The exponent value (0.09) of the V for the  $\sigma_c$  is in good agreement with the 0.08, 0.08, 0.11 values of  $\sigma_t$  obtained by Hu et al.<sup>23</sup> for Sn-0.7Cu-0.7Bi (wt.%) alloy, by Hosch and Napolitano<sup>58</sup> for Al-12wt.%Si alloy, by Çadırılı et al.<sup>59</sup> for Sn-40.5Pb-2.6Sb (wt.%) ternary eutectic alloy respectively. The exponent value (0.16) of the V for the  $\sigma_y$  is in good agreement with the 0.16 value of the  $\sigma_t$  obtained by Hu et al.<sup>23</sup> for Sn-0.7Cu-0.7Bi (wt.%) alloy.

Nevertheless, the exponent value (0.09) of the V for the ultimate compressive strength is higher than the 0.04 value of ultimate tensile strength and the exponent value (0.16) of the V for the compressive yield strength is slightly higher than the 0.12 value of the tensile yield strength,  $\sigma$ , obtained by Hu et al.<sup>23</sup> for Sn-0.7Cu-1.3Bi (wt.%) alloy. Differences exist in the exponent values because of the possible differences in purity, different alloy compositions, solidification conditions and the surface preparation of the test

**Figure 8.** Typical strength-strain curves of Sn-36Bi-22Cu eutectic alloy for different V at a constant G**Figure 9.** Variation of compressive strength of the Sn-36Bi-22Cu alloy as a function of solidification rate

pieces. Also, solidification rate effects the elongation of the alloy. Hu et al.<sup>26</sup> determined that, with increasing solidification rate from 5 to 100  $\mu\text{m/s}$ , the elongation increased from % 28.2 to % 41.5 for Sn-0.7Cu-0.7Bi (wt.%) alloy. Sakuyama et al.<sup>36</sup> found that, the elongation of the Bi-41.8Sn-0.5Cu is higher than the Bi-41.8Sn-0.5Ag, Bi-41.8Sn-0.5Zn and Bi-42Sn alloys. This situations improve the importance of the material for technological applications.

According to the literature<sup>60</sup>, it is well established that the two IMCs are the  $\epsilon$ -phase ( $\text{Cu}_3\text{Sn}$ ) and  $\eta$ -phase ( $\text{Cu}_6\text{Sn}_5$ ). The presence of those intermetallic phases may increase HV and  $\sigma$ , but the ductility properties slightly decrease with further increased solidification rate, that may contribute to a reason. The main reason is that the high growth velocity during directional solidification may result in a radial temperature gradient, which leads to some  $\text{Cu}_3\text{Sn}$  fibers do not grow along with the crystal growth direction. Consequently, the increment in the solidification rate caused finer microstructure. This finer microstructure has improved the some mechanical properties (HV,  $\sigma_c$ ) of the Sn-Bi-Cu ternary eutectic alloy. The crucial role in this solidification process was played

by  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  IMCs in the Sn-matrix of Sn-Bi-Cu ternary system. These IMC phases build a long-range internal stress, resulting in a strengthening effect.

## 4. Conclusions

Sn-36Bi-22Cu (wt.%) ternary eutectic alloy was directionally solidified upwards at a constant temperature gradient (4.2 K/mm) under different solidification rates (8.3-166 $\mu\text{m/s}$ ) in a Bridgman-type directional solidification furnace. The results are summarized as follows:

1. The lamellar spacing and the  $\text{Cu}_3\text{Sn}$  phase spacing decreased with increasing solidification rate. With increasing the solidification rate from 8.3 to 166  $\mu\text{m/s}$ , average  $\lambda$  decreased from 2.81 to 1.46  $\mu\text{m}$ , average  $\lambda_1$  decreased from 103.1 to 22.0  $\mu\text{m}$  for the lamellar spacing and  $\text{Cu}_3\text{Sn}$  phase spacing, respectively. The relationships between the eutectic spacings and solidification rate were obtained by binary regression analysis as ( $\lambda_L = 4.7V^{0.25}$ ,  $\lambda_{LL} = 273V^{0.52}$ )
2. The microhardness increased with increasing solidification rate. Average HV increased from 192.9 to 293.7 MPa, and  $\text{HV}_1$  increased from 2859.1 to 3290.3 MPa with increasing the solidification rate from 8.3 to 166  $\mu\text{m/s}$ . The establishment of the relationship between HV and V can be given as ( $\text{HV} = 367.3V^{0.13}$ ,  $\text{HV} = 3520.5V^{0.04}$ )
3. The compressive strength values increased with increasing solidification rate. The  $\sigma_c$  increased from 102.1 to 139.3 MPa and the  $\sigma_y$  increased from 71.5 to 118.9 MPa with increasing the solidification rate from 8.3 to 166  $\mu\text{m/s}$ . The relationships between  $\sigma$  and V can be given as ( $\sigma_c = 153V^{0.09}$ ,  $\sigma_y = 165V^{0.16}$ ).

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