Tensile Properties of Bi Alloys and a Case Study for Alloy Design in Their Application to High Temperature Solders

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The s-orbital energy levels (ΔMk) of some alloying elements in a Bi cluster model were obtained on the basis of the molecular orbital calculation. In contrast, binary Bi-Cu/-Ag/-Zn system alloys with ΔMk of 0.013–0.343 were manufactured and tension- or hardness-tested, where ΔMk was the compositional average of Mk. The ultimate tensile strength and hardness were improved as alloying elements were added and increased in alloys. There was the relation between the ultimate tensile strength, fracture strain or hardness and ΔMk. Further, the compositions of Bi-2.0Ag-0.5Cu (ΔMk: 0.180), Bi-5.0Ag-0.5Cu (ΔMk: 0.379) and Bi-0.25Cu-0.25Sb (ΔMk: 0.044) were proposed as ternary alloys. It is found that the ultimate tensile strength, fracture strain and hardness values of ternary alloys could be also able to predict using their estimation lines obtained from binary Bi system alloys.

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Keywords: lead-free solders, high-temperature solders, bismuth alloys, tensile strength, alloy design

1. Introduction

In late years, elimination of lead was promoted in industrial fields, according to RoHS (EU Directive on the Restriction of the use of certain Hazardous Substances in electrical and electronic equipment) order and the ELV (End of Life Vehicles) threshold of EU¹. Therefore, the development of lead-free solders was carried out actively in the world. However, the development of lead-free solders for high-temperature applications has not yet advanced²,³. Many research groups paid the attention to the Au–Sn, Zn–Sn and Bi–Ag system alloys as a candidate of lead-free alloys, in the viewpoint of heat, electricity and melting point properties⁴–10. However, Au system alloys were restricted in high temperature solders because of high cost of Au. The application of Zn system alloys was also limited because of oxidability of Zn. On the other hand, the melting point of Bi was 544 K, which was similar with the conventional Pb–Sn alloys. Moreover, Bi possessed not only cheap cost but also no harm to human bodies and environment. Bi system alloys were one of candidate of lead-free alloys for high-temperature solders with great promise¹¹,¹².

So far, the development of alloys with high performance had been performed relying on many trial-and error experiments and a few empirical rules. In order to develop new alloys more efficiently, a theoretical approach was strongly needed for the alloys design. The d-electrons concept on the basis of the theoretical calculation of electronic structures of alloys had been proposed on the basis of the Discrete Variational (DV)-Xα¹³–¹⁵ cluster calculation, by Morinaga et al¹⁶,¹⁷. This concept was devised at first for austenitic Ni, Co and Fe alloys, and phase boundary or some physical or chemical properties were predicted by electronic parameters. The two parameters, Bo and Md, were used in this approach. The Bo which was the bond order showed the overlapping of electron clouds between atoms. Therefore, it was a measure of the covalent bond strength between atoms. The covalency increased with increasing Bo. The value of Md was related to the charge transfer, and hence to the electronegativity of elements. The Md was also found to be associated with the atomic radius. Both the electronegativity and the atomic radius were classical parameters which have been used in describing the nature of the chemical bond between atoms in solids.

The concept of alloys design had spread over the world since 1964 when PHACOMP (Phase Computation) had been proposed¹⁸. This was a prediction method for the appearance of the undesirable brittle phases in the face-centered cubic (fcc) matrix. The parameter used for this prediction is electron vacancy number (Nv) that was the number of vacancies or electron holes existing above the Fermi level in the metal d-band proposed by Pauling¹⁰. The solid solubility problem of alloys had been treated by the classical parameters of electronegativity and the atomic radius. The solid solubilities in transition-metal based fcc alloys could be treated quantitatively using the Md parameter, compared with the prediction by Nv²⁰. Therefore, Md-PHACOMP had been to be superior to the current Nv-PHACOMP²⁰. Ti alloys were classified into the α, α+β and β types according to the phases existing in alloys. Compositions of forty commercial alloys were plotted on the Bo and Md coordinates. These three types of alloys were clearly separated in the Bo and Md map¹⁹. Moreover, the compositional optimization of Al¹²¹ system alloys as a simple metal were carried out by using s-orbital energy level (ΔMk)¹³–¹⁵. The interaction between the dislocation density (or hindrance for dislocation migration) and ΔMk were investigated in the previous report¹¹. It was concluded that the ΔMk could be used as the indication of solid solution harden-
ing level for ternary Al-1.5Mn-xMg alloys.

In this paper, DV-Xα cluster method was also used to obtain the s-orbital energy levels (\(M_k\)) of some alloying elements in a Bi cluster. In contrast, the tensile properties were measured using binary Bi-Cu/-Ag/-Zn alloys with a eutectic system. Their tensile and hardness properties were tried to arrange by this electronic parameter, as well as Ni, Al, Ti alloys. Further, the ternary Bi system alloys were proposed and arranged by this parameter. The possibility for the prediction of the mechanical properties by this parameter was explored, as case study of Bi alloy design for the high temperature application.

2. Compositions of Alloys

2.1 Electronic parameter representing alloying effects

The \(M_k\) parameter was calculated in the cluster (MBi7) presenting by an octahedron as a model of triclinic Bi. This cluster was shown in Fig. 1, and contained an alloying element M and its surrounding Bi atoms. Therefore, the alloying effects were inevitably involved in this \(M_k\) parameter. The values of \(M_k\) for alloying elements were listed in Table 1. Furthermore, as shown in Figs. 2 and 3, it was associated with the electronegativity and the atomic radius of elements: namely, the \(M_k\) level decreased with increasing electronegativity of pure metals, whereas it increased with increasing the atomic radius, even though there were some differences in the correlations between transition metals and non-transition metals, which agreed with the relation obtained from the MAI_{18} cluster as a model of fcc Al. As explained in reference, it was well known that the energy level obtained by the \(\chi_\alpha\) calculation represented the electronegativity itself. In addition, the p-orbital energy level may be employed instead of the s-orbital energy level, but the spherical symmetrical s-orbital was probably better for the estimation of the mechanical properties of alloys, compared with the directional p-orbital.

Employing \(M_k\) parameters, the \(\Delta M_k\) in the case of Bi alloys was defined using compositional average, as follow expression (1).

\[
\Delta M_k = \Sigma X_M |M_k(M) - M_k(Bi)|
\]

where, \(X_M\) was the molar fraction of alloy element M, \(M_k(M)\) was the \(M_k\) of alloy element M, and \(M_k(Bi)\) was the \(M_k\) of mother metal Bi.

2.2 Selection of experimentally binary and ternary alloys

The eutectic compositions of Bi-0.15mass%Cu, Bi-2.5mass%Ag and Bi-2.7mass%Zn binary alloys were chosen.

![Fig. 1](image1.png)  
Fig. 1 A cluster model used for the calculation; M is alloying element.

![Fig. 2](image2.png)  
Fig. 2 Relation between the atomic radius and \(M_k\) of transition metals or non-transition metals added in a Bi cluster model.

<table>
<thead>
<tr>
<th>Elements</th>
<th>(M_k) (eV)</th>
<th>Elements</th>
<th>(M_k) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0.92</td>
<td>Ge</td>
<td>-8.36</td>
</tr>
<tr>
<td>Ag</td>
<td>4.63</td>
<td>Ti</td>
<td>6.10</td>
</tr>
<tr>
<td>Cu</td>
<td>3.47</td>
<td>Ca</td>
<td>6.25</td>
</tr>
<tr>
<td>Sn</td>
<td>4.54</td>
<td>Fe</td>
<td>4.20</td>
</tr>
<tr>
<td>Mo</td>
<td>5.43</td>
<td>Ni</td>
<td>3.88</td>
</tr>
<tr>
<td>Mn</td>
<td>4.48</td>
<td>Bi</td>
<td>0.92</td>
</tr>
<tr>
<td>Zn</td>
<td>2.40</td>
<td>Si</td>
<td>1.09</td>
</tr>
<tr>
<td>In</td>
<td>-4.11</td>
<td>K</td>
<td>9.17</td>
</tr>
<tr>
<td>Zr</td>
<td>6.24</td>
<td>Mg</td>
<td>4.06</td>
</tr>
<tr>
<td>Ga</td>
<td>1.27</td>
<td>V</td>
<td>5.03</td>
</tr>
<tr>
<td>Co</td>
<td>4.00</td>
<td>Sc</td>
<td>6.01</td>
</tr>
<tr>
<td>Cr</td>
<td>4.48</td>
<td>Li</td>
<td>6.50</td>
</tr>
<tr>
<td>Al</td>
<td>1.98</td>
<td>Be</td>
<td>2.46</td>
</tr>
<tr>
<td>Na</td>
<td>6.78</td>
<td>Nb</td>
<td>5.69</td>
</tr>
</tbody>
</table>

![Fig. 3](image3.png)  
Fig. 3 Relation between the electronegativity and \(M_k\) level of transition metals or non-transition metals added in a Bi cluster model.
because of both the low melting temperature and a little amount of ductility by the fine crystallized phases caused in a eutectic reaction. In contrast, pure Cu and Ag with fcc have many slip systems, and Zn was one candidate as high temperature solders. These eutectics exist near to pure Bi at temperatures about 1–16 K below the melting point of Bi, which suggests a little amount reduction in melting points even by the addition of ternary alloying elements in their alloy systems. Further, the alloy compositions near eutectic compositions were also chosen in this study, as listed in Table 2. The values of $\Delta M_k$ were also listed in this table. Moreover, Bi and Sb were unlimited miscible elements in solid, and Cu, Ag and Sb were chosen as ternary alloy elements. $\Delta M_k$ of ternary Bi system alloys was decided to be less than 0.400, adjusting by amount of ternary alloys elements, as mentioned in the term of 4.2.1. The ternary alloys were proposed for the investigation of relation between ultimate tensile strength or fracture strain and the $\Delta M_k$ level, which compositions were listed in Table 3.

3. Experiment Procedure

3.1 Materials and manufacturing process

The stick Bi (99.99% of purity), the granular Ag (99.99% of purity), the laminar Cu (99.99% of purity), the granular Zn (99.99% of purity) and the granular Sb (99.99% of purity) were put into the graphite crucible, and it was set in the electric furnace in air. Bi had the 2–3 mm diameter and the others had the 1 mm thickness. The molten metal was mixed by a ceramic stick at 773 K, and held at this temperature for 1.8 ks, after the melt down of all raw materials. And then the molten metal was poured into the casting mold which was heated to 773 K. The ingot was air cooled to 293 K.

3.2 Evaluation of some properties

Microstructural observation of these alloys using as-cast samples by the SEM and quantitative analyses of elements were conducted by the electron probe micro-analyzer (EPMA; JEOL JXA-8200, Japan). Tensile tests of the experimental alloys were performed at 293 K and 423 K in air by using a mechanical testing machine (Autograph DCS-R-5000, Shimadzu Corporation, Japan) at the initial strain rate of $3.4 \times 10^{-1} \text{ s}^{-1}$.

4. Results and Discussion

4.1 Characteristics on binary Bi-Cu/Ag/Zn alloys

4.1.1 Microstructures

The microstructures of as-cast alloys with binary elements of Cu, Ag and Zn were shown in Fig. 4. Pure Bi showed a mono-phase of Bi and equi-axial grains. Primary Cu and eutectic of Bi and Cu were observed in Bi-0.5 and 1.0Cu. The amount and size of primary Cu in Bi-1.0Cu were larger than those of Bi-0.5Cu, which led the lower value in fracture strain, as mentioned in the term of 4.1.2.

Primary Ag solid solution (hereafter called Ag S.S.) and eutectic of Bi and Ag S.S. were observed in Bi-5.0Ag. In contrast, the eutectic of Bi and Ag S.S. were just observed in Bi-2.5Ag. Primary Zn and eutectic of Bi S.S. and Zn were observed in Bi-3.7Zn. In contrast, primary Bi S.S. with the dendritic shape and eutectic of Bi S.S. and Zn were observed in Bi-1.8Zn. The primary phases with plate and rod like shape were crystallized in Bi-1.0Cu, -5.0Ag and -3.7Zn alloys, which resulted in lower values in the fracture strains, as mentioned in the term of 4.1.2.

For their experimental alloys, the grain size of matrix was measured by the linear intercept method. The mean grain sizes were listed in Table 2, their values were 37 to 43 $\mu$m, showing the almost same level due to the usage of the same solidification condition. The microstructure of the Bi-2.5Ag alloy showed a typical Bi-Ag eutectic structure with the Bi and Ag solid solution formed alternately in normal eutectic cells with the size of 200 $\mu$m, as seen in Fig. 4 (d). The distance of their interphases was approximately 4.5 $\mu$m in the eutectic cells. In contrast, pure Bi showed the grain size of 45 $\mu$m.

For the quantitative analyses of alloying elements, the EPMA method was simply employed for convenience. Bi-1.0Cu, Bi-1.8Zn and Bi-5.0Ag-0.5Cu in nominal compositions were measured as Bi-1.0Cu, Bi-1.7Zn and Bi-4.8Ag-0.5Cu, respectively. Therefore, nominal compositions were almost same to chemical ones, and used for the alloy-description in this paper.

4.1.2 Tensile properties at 293 K

Figures 5 and 6 showed the nominal stress-strain curves of 9 binary Bi-M alloys and pure Bi as a reference, obtained from tensile tests at 293 K. The behavior in the stress-strain curves were changed depending on the kinds and amount of their alloying elements. As shown in Fig. 5, the pure Bi showed a little amount of plastic deformation after elastic de-

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**Table 2** The nominal compositions of binary Bi system alloys, their $\Delta M_k$ and their mean grain sizes.

<table>
<thead>
<tr>
<th>Alloys (mass. %)</th>
<th>Alloys (mol%)</th>
<th>$\Delta M_k$</th>
<th>Mean grain size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-0.15Cu</td>
<td>Bi-0.5Cu</td>
<td>0.013</td>
<td>42</td>
</tr>
<tr>
<td>Bi-0.25Cu</td>
<td>Bi-0.8Cu</td>
<td>0.021</td>
<td>42</td>
</tr>
<tr>
<td>Bi-0.5Cu</td>
<td>Bi-1.6Cu</td>
<td>0.042</td>
<td>43</td>
</tr>
<tr>
<td>Bi-0.75Cu</td>
<td>Bi-2.4Cu</td>
<td>0.062</td>
<td>41</td>
</tr>
<tr>
<td>Bi-1.0Cu</td>
<td>Bi-3.2Cu</td>
<td>0.082</td>
<td>37</td>
</tr>
<tr>
<td>Bi-2.5Ag</td>
<td>Bi-4.7Ag</td>
<td>0.176</td>
<td>——</td>
</tr>
<tr>
<td>Bi-5.0Ag</td>
<td>Bi-9.2Ag</td>
<td>0.343</td>
<td>40</td>
</tr>
<tr>
<td>Bi-1.8Zn</td>
<td>Bi-5.6Zn</td>
<td>0.082</td>
<td>40</td>
</tr>
<tr>
<td>Bi-3.7Zn</td>
<td>Bi-11.0Zn</td>
<td>0.163</td>
<td>41</td>
</tr>
</tbody>
</table>

**Table 3** The nominal compositions of ternary Bi system alloys, their $\Delta M_k$ and their mean grain sizes.

<table>
<thead>
<tr>
<th>Alloys (mass. %)</th>
<th>Alloys (mol%)</th>
<th>$\Delta M_k$</th>
<th>Mean grain size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-2.0Ag-0.5Cu</td>
<td>Bi-3.8Ag-1.6Cu</td>
<td>0.180</td>
<td>39</td>
</tr>
<tr>
<td>Bi-5.0Ag-0.5Cu</td>
<td>Bi-9.2Ag-1.6Cu</td>
<td>0.379</td>
<td>43</td>
</tr>
<tr>
<td>Bi-0.25Cu-0.25Sb</td>
<td>Bi-0.8Cu-0.4Sb</td>
<td>0.044</td>
<td>40</td>
</tr>
</tbody>
</table>
formation, and values of the ultimate tensile strength or fracture stress, and fracture strain were 12 MPa and 0.7%, respectively. Moreover, the values in the ultimate tensile strength of Bi-0.15Cu, Bi-0.25Cu, Bi-0.5Cu, Bi-0.75Cu, Bi-1.0Cu, Bi-2.5Ag, Bi-5.0Ag, Bi-1.8Zn, Bi-3.7Zn alloys were 1.1 to 2.5-times larger than that of pure Bi, in 5 alloys showing the low fracture strain less than 4.6%. In contrast, the values in the ultimate tensile strength of Bi-0.25/0.5/0.75Cu and Bi-1.8Zn alloys were 1.2 to 1.4-times larger than that of pure Bi, in 4 alloys showing the larger values more than 9–33% in fracture strain, as shown in Fig. 6 indicating the full curves of stress and strain to fracture. The reduction of area was also indicated in this figure. The pure Bi showed lowest value in the reduction of area, which corresponded to the fracture strain of 0.7%. In contrast, the heterogeneity plastic deformation in three dimensions was observed showing the reduction of area of 4.3–40.7%, in the Bi-0.5Cu alloy with the highest fracture strain of 33%.

Some fracture surfaces after tensile tests were shown in Fig. 7, as typical examples. The pure Bi and Bi-1.0Cu samples with the lowest value of 0.7% in fracture strain, were fully exhibited the typically intra-granular brittle fracture mode showing the cleavage patterns in Bi grains. In contrast, Bi-0.5Cu with the highest value of 33% in fracture strain, did not only showed brittle fracture region, but also showed the secondary cracks and the curvature fracture surfaces, showing the plastic deformed outer rim with the reduction of area 4.3–40.7% as shown in Fig. 6. The secondary cracks and the curvature fracture surfaces were caused in deformable Cu parts. The microstructural characteristics including of the
morphology and amount of the Cu phase were important because of the sensitivity of microstructure to the plastic deformation amount. The fracture strain behaviors could be comparable among each alloy, because each alloy was manufactured at the same conditions. Further, Bi-1.8Zn with the moderate value of 6.7% in fracture strain, showed the curvature edge in cleavage planes, which resulted from the dispersion of pure Zn particles and formation of Bi-Zn S.S.

4.1.3 $\Delta Mk$ parameter and mechanical properties

Figure 8 shows the relation between values in Rockwell hardness number on B scale and $\Delta Mk$ for binary alloys. The hardness was increased as the $\Delta Mk$ or the amount of alloying elements were increased in alloys. It is roughly found that the hardness of binary alloys depended on the mixture rule on the basis of that in construction phases. Where, the value of HRB in pure Cu was 90. There was the linear relation between the hardness and $\Delta Mk$ in Mg alloys with dual phases as a simple metal\(^{28}\). In contrast, the hardness values were almost constant in the region of $\Delta Mk$ more than 0.17. Further study is needed in order to understand the relation between the hardness and $\Delta Mk$ in a more microstructural approach.

Figure 9 shows the relation between 0.2% proof stress, ultimate tensile strength or fracture strain and $\Delta Mk$. The values of the 0.2% proof stress of Bi-0.15Cu, Bi-0.25Cu, Bi-0.5Cu, Bi-0.75Cu, Bi-1.0Cu, Bi-1.8Zn, Bi-3.7Zn, Bi-2.5Ag and Bi-5.0Ag were 8.0, 6.8, 7.1, 9.9, 12.5, 10.0, 18.1, 16.3 and 18.6 MPa, respectively. Figure 9 shows that the 0.2% proof stress of binary Bi system alloys were increased with increasing of $\Delta Mk$ to approximately 0.17, regardless of kinds of alloying elements. And then the 0.2% proof stress became to almost constant with increasing of $\Delta Mk$ more than 0.17. In contrast, the relationship between ultimate tensile strength and $\Delta Mk$ of binary system alloys was same as that obtained from the 0.2% proof stress. The value of 0.2% proof stress of pure Bi was 7.5 MPa. It was also plotted in this figure. It is interesting that the values in the measured both strength of pure Bi agreed with the values which were obtained by extrapolation to $\Delta Mk$ of zero using the predicted line for the both strength in binary alloys.

The behavior of 0.2% proof stress and ultimate tensile strength to $\Delta Mk$ was almost same as that obtained from the hardness. As shown in Table 2, the values of mean grain sizes were almost same among experimental alloys, which corresponded to the same level for their grain boundary strengthening. It may be considered that there were different levels among the solid solution strengthening of experimental alloys. The me-
The mechanical properties of both tension and hardness might be also represented by $\Delta M k$ in Bi alloys, which agreed with the results obtained from Mg and Sn alloys\(^ {14,28}\). In contrast, the maximum values, 25 and 33%, in the fracture strain were shown in Bi-0.25Cu and 0.5Cu alloys with $\Delta M k$ of 0.021 and 0.042, respectively.

It may be considered on the basis of the fracture behaviors, that the deformation of Bi alloys depended on both patterns of the intra-granular brittle fracture in pure Bi grains and deformable fracture in or near metallic grains of Cu, Ag and Zn by the stress relief in crack propagation. This fracture behaviors are similar to those of the composites consisting of ceramics/metals with nano-size, showing the improvement in fracture toughness values due to the presence of metallic parts\(^ {29}\). Therefore, it may be considered that maximum values in fracture strain were shown by the optimization in both the size and amount of Cu particles in eutectic regions in Bi-0.25 and 0.5 Cu alloys.

There were the Bi area as a continuous phase and little amounts of deformable metallic particles such as Cu, Ag and Zn in alloys. This meant to predominant action for plastic deformation by both the solid solution hardening and grain boundary hardening of their metallic particles, because of limited deformation in Bi grains. It may be considered that their hardening mechanisms correlate to $\Delta M k$. Actually, in previous work, $\Delta M k$ varied linearly with the 0.2% proof stress and tensile strength of commercially available wrought Al alloys (1000–7000 series) with multiple components\(^ {22,28}\). Strength properties including both strain hardening and precipitation hardening were treated well in terms of this parameter alone\(^ {22,28}\). Further, it has been concluded that the interaction between the proof stress and dislocation density or hindrance for dislocation migration at the constant strain could be explained by $\Delta M k$, which might lead to the indication of solid solution hardening level using this parameter for Al-1.5Mn-X ternary alloys\(^ {21}\). Therefore, it may be presumed even under this condition of few or no solubility of each element into Bi, that the mechanical properties were roughly predicted by the values of $\Delta M k$ considering on the basis of fracture behaviors, because this parameter correlated to dislocation behaviors such as hindrance for dislocation migration in or near metallic parts by the increase or addition of alloying elements. Further study is greatly needed in order to understand the present $\Delta M k$ approach in a more fundamental manner such as the observation of dislocation behaviors by TEM.

### 4.2 Characteristics of ternary Bi alloys

#### 4.2.1 Microstructures

Bi-0.25Cu-0.25Sb, Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu with $\Delta M k$ of 0.044, 0.180 and 0.379 as ternary alloys, respectively, were cast in metallic molds. Their microstructures are also shown in Fig. 4. The primary Ag S.S. and eutectic of Bi, Ag S.S. and Cu S.S. were observed in Bi-5.0Ag-0.5Cu. The primary Bi with the dendritic shape and eutectic of Bi, Ag S.S. and Cu S.S. were observed in Bi-2.0Ag-0.5Cu. In contrast, the primary Cu S.S., eutectic of Bi-Sb and Cu S.S. was observed in Bi-0.25Cu-0.25Sb. In particular, the large amount and size of primary phases with the rod like shape in Bi-5.0Ag-0.5Cu led the lower value in fracture strain, compared with Bi-2.0Ag-0.5Cu of a same alloying system, as mentioned in the term of 4.2.2. For their ternary alloys, the grain size of matrix was measured by the linear intercept method. The mean grain sizes were listed in Table 3, their values were 39 to 43 $\mu$m. Therefore, it is found that the values of mean grain sizes were measured in the almost same level among all experimental alloys.

#### 4.2.2 Mechanical properties

Ternary alloys were tensile tested and their results were shown in Figs. 6 and 10. Their alloys showed the improved flow stress and strain, compared with pure Bi. Their 0.2% proof stress, ultimate tensile strength and fracture strain were also replotted in Fig. 9. It is found that both strength and fracture strain of ternary alloys could be also predicted using their estimation lines obtained from binary Bi system alloys.

The Bi-0.25Cu-0.25Sb alloy with fracture strain of 12% showed both the straight and unevenness fracture surfaces meaning the brittle and deformable patterns, respectively, as shown in Fig. 7 (f), (l). This alloy showed the reduction of area of 5.6–30.3%, which resulted in the heterogeneity of plastic deformation in three dimension, as shown in Fig. 6. In contrast, Bi-2.0Ag-0.5Cu with the moderate value of approximate 5% in fracture strain, showed the limited region showing unevenness fracture surfaces and minimized fracture units, as seen in Fig. 7 (e), (k).

In contrast, the hardness values of three kinds of ternary alloys were also plotted in Fig. 8. Their alloys showed higher values in hardness as the $\Delta M k$ was increased in ternary alloys. Each value in mechanical properties such as tension and hardness for ternary alloys agreed with their estimation lines obtained from binary alloys, mentioned above. It may be convenient in future that the prediction of mechanical properties by the $\Delta M k$ is applied to Bi system alloys with multiple components more than three elements. Actually, the Bi-2Ag-0.5Cu became to a promising alloy as one of high temperature solders which have to satisfy mechanical properties of 20MPa-UTS and 5%-fracture strain at 293 K\(^ {30}\). Also, the Bi-2Ag-0.5Cu alloy showed the good impact, melt-down and wettability properties\(^ {30}\), which might lead to the alternative by this alloy for Pb-5/10Sn alloys. There are still several remaining questions to be solved, even though $\Delta M k$ is indeed a convenient parameter in estimating the mechanical properties of Bi alloys.

![Fig. 10 Stress-strain curves of Bi-2.0Ag-0.5Cu, Bi-5.0Ag-0.5Cu alloys and pure Bi.](image-url)
4.3 Tensile properties at 423 K

Figure 11 showed the stress-strain curves of Bi-0.15Cu, Bi-0.5Cu, Bi-0.75Cu and Bi-5.0Ag-0.5Cu as typical experimental alloys or pure Bi as a reference. The tensile tests were conducted at 423 K. As shown in this figure, the values of the ultimate tensile strength of pure Bi, Bi-0.15Cu, Bi-0.5Cu, Bi-0.75Cu and Bi-5.0Ag-0.5Cu with $\Delta M_k$ of 0.000, 0.013, 0.042, 0.062 and 0.379 were 4.2, 4.4, 5.2, 5.8 and 8.7 MPa, respectively. In contrast, the values of the 0.2% proof stress of pure Bi, Bi-0.15Cu, Bi-0.5Cu, Bi-0.75Cu and Bi-5.0Ag-0.5Cu were 3.8, 3.9, 4.2, 4.5 and 7.8 MPa, respectively. Both 0.2% proof stress and ultimate tensile strength of these alloys were decreased, compared with the values at 293 K because of the softening at 423 K, which corresponded to the typically stress-strain behavior at high temperatures. Both strength of their alloys increased as $\Delta M_k$ values increased, which corresponded to the results obtained from the room temperature tests, as shown in Fig. 9 (a). These 5 alloys revealed excellent ductility at this high temperature test condition. The values in the fracture strain of pure Bi, Bi-0.15Cu, Bi-0.5Cu, Bi-0.75Cu and Bi-5.0Ag-0.5Cu were 15.4, 30.5, 45.6, 35.9 and 32.3%. The minimum and maximum values in the reduction of area were also indicated in this figure. The pure Bi showed the lowest value in the reduction of area, which corresponded to the fracture strain of 15.4%. In contrast, the Bi-0.5Cu alloy with the highest fracture strain of 45.6%, showed was the highest value of 80-93% in the reduction of area. The Bi-0.5Cu alloy with $\Delta M_k$ of 0.042 showed the highest fracture strain also at 423 K, which corresponded to its maximum value in the fracture strain at 293 K as shown in Fig. 9 (b).

Fracture surfaces of pure Bi and Bi-0.75Cu after tensile tests were shown in Fig. 12, as typical examples. The pure Bi with the lowest value of 15.4% in fracture strain, showed the intergranular fracture mode with a little curvature surface. In contrast, Bi-0.75Cu with the value of 35.9% in fracture strain, showed the excellent ductility showing the three dimensionally heterogeneous necking.

5. Conclusions

(1) Cu, Ag and Zn were chosen as binary elements in Bi system alloys, their alloys with compositions near the eutectic and their values of $\Delta M_k$ were from 0.013 to 0.343. The ultimate tensile strength and fracture strain were higher than those of pure Bi. The ultimate tensile strength of binary Bi system alloys were increased with increasing of $\Delta M_k$ until approximately 0.17, regardless of the kinds and amount of alloying elements. Then the ultimate tensile strength became to almost constant in the range of $\Delta M_k$ more than 0.17. In contrast, the maximum values, 25 and 33%, in the fracture strain were shown in Bi-0.25Cu and -0.5Cu alloys with $\Delta M_k$ of 0.021 and 0.042, respectively. The mechanical properties such as tension and hardness were roughly predicted by the values of $\Delta M_k$.

(2) The proposed Bi-0.25Cu-0.25Sb, Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu with $\Delta M_k$ of 0.044, 0.180 and 0.379 as ternary alloys, respectively, showed the improved tension and hardness properties, compared with pure Bi. It is found that their ultimate tensile strength, fracture strain and hardness values could be also predicted using their estimation lines obtained from binary Bi system alloys.

(3) There are still several remaining questions to be solved, even though $\Delta M_k$ is indeed a convenient parameter in the prediction of the mechanical properties of binary and ternary Bi alloys. This prediction may lead to the efficient alloy-design of Bi solders for high temperature applications.

(4) Both 0.2% proof stress and ultimate tensile strength at 423 K for selected alloys were decreased due to the softening, compared with their values at 293 K, which corresponded to the typically stress-strain behavior at high temperatures.

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