Effects of sulfur and tin contents on hardness of copper-tin alloy under reduced atmosphere in sintering process

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Abstract
Sintered materials are commonly used in industrial equipment, including bearing components. These materials include bimetals consisting of steel backed sintered bronze lined bushings. In particular, 90Cu–10Sn (mass%) bronze is widely used in bearing components. Lead bronze, in which the lead serves as a solid lubricant, is being replaced with other materials, among which are sulfide-dispersed bronzes. In sulfide-dispersed bronze, sulfides instead of lead play the role of solid lubricant. However, the sulfides in the bronze may be subject to chemical reduction during sintering, especially when this is carried out under a reducing atmosphere containing hydrogen gas. In this study, we investigate the effect of the sulfides on the bronze, with a focus on the hardness of the bronze matrix and the reaction between sulfides and hydrogen gas. Water-atomized powders were prepared for comparison of the sintering behavior. The sintering temperature in the tests was 1123 K. From the phase diagram of the Cu–Sn system, the liquid phase starts to form into bronze containing 20 mass% Sn at approximately 1123 K; thus, some conditions undergo liquid-phase sintering. Sulfides are observed to disappear from sintered bronze surfaces under a reducing atmosphere. However, the sulfides that are not in a solid solution do not affect the hardness of the bronze matrix, which does, however, depend on the tin content.

Key words : Cu alloy, Cu-Sn system, Sintering atmosphere, Powder metallurgy, Sulfides, Hardness

1. Introduction

Alloys based on copper (Cu) and tin (Sn), i.e. bronzes, are useful materials. For example, sliding bearings made of bronze are common in industrial applications. These bearings are often manufactured using a sintering process. In particular, 90Cu–10Sn (mass%) bronze is widely used in bearing components. There are several ways to produce the 90Cu–10Sn alloy. Mixing electrolytic copper powders and tin powders is a well known and long-standing approach. Following the development of suitable atomized copper powders, these became useful candidates for mixing with tin powders. The historical background is well described by Berry (Berry, 1972). Price and Oakley (Price and Oakley, 1965) examined partially alloyed powders and pre-alloyed atomized bronze powders with a view to their possible use in high-density bronze components. If sintered bronze is to be used to make a sliding component, it must satisfy certain requirements regarding predetermined size, mechanical properties, heat conductivity and antifriction capability. However, there are many variable factors affecting these properties. First of all, there is a choice among different powder species, as described above. At the compacting stage, the die size and compacting pressure are selectable. There is also the well-known method of cladding steel with this alloy during the production of bimetallic strips by rolling. At the sintering stage, sintering temperature, heating rate, cooling rate and atmosphere are selectable. From these complex conditions, a suitable
combination must be selected for each application.

Berry (Berry, 1972) examined the sintering of atomized copper-phosphorus and tin powders under various conditions, and concluded that swelling of a sintered workpiece was sensitive to the phosphorus content of the copper, the fineness of the tin powder, the addition of pre-alloyed bronze, the green density, the heating rate, the furnace atmosphere and the sintering temperature. With regard to the sintering atmosphere, Mitani (Mitani, 1962) concluded that abnormal growth could be decreased by using a nitrogen atmosphere with minimal hydrogen content, since his findings indicated that a significant proportion of the expansion was caused by evolution of dissolved hydrogen on solidification. In some cases, nitrogen gas alone is used for sintering (Moshksar, 1993). Acharya and Mukunda (Acharya and Mukunda, 1982) reported that sintering bronze in vacuum was preferable to the use of a reducing atmosphere in terms of providing better mechanical properties such as radial crushing strength. They (Acharya and Mukunda, 1988) also developed a phase identification method to investigate changes in bronze phases during the sintering process. For the very high stress bearings of car engines, leaded laminated bronzes (25 % or more lead) are used in the form of a thin layer poured on the steel. Traditionally, such bearings have been made in a bimetallic form consisting of sintered copper alloys on steels. In some cases, the sintered layer is coated with a second layer of Sn. Recently, however, several countries have adopted regulations that prevent the use of lead in engineering equipment, thereby necessitating the development of lead-free materials. This has motivated the development of several lead-free materials for bearing production. Candidates for lead-free Cu–Sn systems include Cu–Sn–Bi and Cu–Sn–Ni, and their sinterability and recrystallisation have been determined (Pacheco and Campos, 2012).

Sulfide-dispersed bronze has been also developed as a candidate for lead-free bronze (Wakai, et al., 2007), (Maruyama, et al., 2008). In sulfide-dispersed bronze, sulfides (instead of lead) play the role of solid lubricant (Sato et al., 2012). MoS$_2$ and WS$_2$ are commonly used as sulfides in sintered bronze. Kumar et al. (Kumar, et al., 2013) investigated the dry sliding friction and wear characteristics of Cu–Sn alloy containing MoS$_2$. Rapoport et al. (Rapoport, et al.,2001) reported that bronze–graphite nanocomposites impregnated with oil and fullerene-like WS$_2$ nanoparticles exhibited very low friction coefficients and low wear rates over a wide range of the pressure–velocity parameter.

Sulfide-dispersed bronzes are useful for sintering, but there is concern that sulfides may react with the reducing gas (mainly hydrogen). As already mentioned, Mitani (Mitani, 1962) reported that one of the reasons for abnormal expansion is the presence of hydrogen gas. It may be difficult for engineers to estimate the strength of Cu–Sn materials with or without lead, because sintering of Cu–Sn is a complex process involving a number of variable factors: Cu and Sn composition, sintering temperature and time, and sintering atmosphere. For example, Cu–Sn–Ni and Cu–Sn–Bi sintered satisfactorily at 1093 K and 1173 K, respectively, according to Pacheco and Campos (Pacheco and Campos, 2012). In addition, after recrystallisation by heat treatment, both alloys satisfied hardness requirements for use in friction bearings. Tandon et al. (Tandon, et al.,1995) conducted experiments on Cu–Sn alloy systems to demonstrate the densification sequence during particle fragmentation. The manufacturing process of some bearings commonly involves sintering under a reducing atmosphere such as hydrogen gas. In the case of Cu alloys containing sulfides, sulphur may react with the reducing gas and disappear from the alloy. Because sulphur reacts with hydrogen to hydrogen sulfide. Moreover, the mechanical properties of such sintered Cu–Sn–S materials have not been determined.

In this study, we investigate the effect of sulfides on bronze that has already been atomized, focusing specifically on the strength of the bronze matrix and the reaction between sulfides and hydrogen gas, as well as determining the optimal composition and atmosphere for sintering sulfide-dispersed bronze. Solid-state and liquid-phase sintering are compared under reducing and inert atmospheres. Hardness as one of the important mechanical properties is also investigated. It is common in manufacturing procedures to mix graphite and penetrating oils into bronze. However, we do not use these additives in this study, because we wish to concentrate here on the effects of sulfide and sintering conditions.

2. Materials

Water-atomized powders were prepared for comparison of the sintering behavior. As is usual in the preparation of sulfide-dispersed Cu–Sn materials, the sulfide was pre-alloyed by water atomization (Nippon Atomized Metal Powders Corporation). As shown in Fig. 1a, micro-sized small dots were observed under scanning electron microscopy (SEM); this image is a sectional view of one of the typical bronze-containing sulfides (irregular powders). Generally, sintered composites obtained from premixed bronze and sulfides exhibit poorer mechanical properties, although it has been
reported that mechanical properties are improved if the MoS\(_2\) particles are coated with copper (Shikata, et al., 1985). However, the sulfide-dispersed bronze in this investigation was made by atomizing a pre-alloyed material. Thus, it may be that pre-alloyed materials have better mechanical properties than premixed materials. To determine the elemental composition of the observed small dots, we conducted energy-dispersive X-ray spectroscopy (EDS). A ternary sulfide composed of Cu, Fe and S was detected, as can be seen in Fig. 1. This sulfide is a type of bornite (\(\text{Cu}_5\text{FeS}_4\)), as shown by X-ray diffraction (Sato, et al., 2014).

### 3. Experimental method

#### 3.1 Sintering and manufacturing process

Bimetal specimens were prepared as follows:

1. Powder spraying: Powder was sprayed to a thickness of 1.0 mm (by levelling off) onto a 3.2-mm-thick steel plate (low-carbon steel), without an admixture of binding materials such as oils or zinc stearate.

2. First sintering under a reducing (H\(_2\) and N\(_2\)) and/or inert (N\(_2\)) atmosphere: The samples were heated to 1123 K for 1050 s in a Koyo Thermo Systems 810A-II mesh belt furnace.

3. Rolling: The bimetal thickness was adjusted by a cold rolling machine. The thickness of the bimetal was adjusted so that the entire surface of the Cu side of the bimetal was in contact with the roller surface.

4. Second sintering under a reducing and/or inert atmosphere: The samples were heated to 1123 K for 1368 s in a Koyo Thermos Systems 810A-II mesh belt furnace.

Following these procedures, for the analysis of mechanical properties, hardness tests only were conducted, because the bimetals and sintered copper alloy specimens were too thin to be subjected to tensile tests. The hardness of the sintered copper alloy specimens was evaluated using a Vickers hardness tester. The indenter was pushed into the matrix of the copper alloy and the steels under an applied load of 0.98 N for 10 s. Measurements of the hardness had conducted five times for every specimens at random positions which was not interference each other.

#### 3.2 Test specimens

Six test specimens were prepared for observation of the sintering process, as shown in Table 1, in which the chemical
composition is described only for the primary elements (i.e. Cu, Sn, Fe, S and sulfide). Here, with regard to the sulfide concentration, all sulphur was assumed to exist as bornite (Cu$_5$FeS$_4$). SB8 (sulfide bronze containing 8 mass% Sn), SB10 and SB12 were used as the single pre-alloyed powders for solid-state sintering at the first sintering. However, SBP8 (sulfide bronze from a premix containing 8 mass% Sn), SBP10 and SBP12 were prepared as mixtures of two kinds of powders: the same pre-alloyed powders used in the first sintering (i.e. SB8, SB10 and SB12) and bronze (containing 20 mass% Sn) powders. These mixed powders were prepared for liquid-phase sintering in the first sintering. The addition of low-melting-point Cu–Sn powders in the sintering processes, which also increases the sintering properties, has also been investigated experimentally (Tosangthum, et al., 2008).

Table 1 Chemical composition according to primary elements (mass%)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Notation</th>
<th>Cu</th>
<th>Sn</th>
<th>Fe</th>
<th>S</th>
<th>Sulfide</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB</td>
<td>8</td>
<td>Balance</td>
<td>7.90</td>
<td>0.18</td>
<td>0.31</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Balance</td>
<td>9.52</td>
<td>0.38</td>
<td>0.48</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Balance</td>
<td>12.00</td>
<td>0.41</td>
<td>0.58</td>
<td>2.27</td>
</tr>
<tr>
<td>SBP</td>
<td>8</td>
<td>Balance</td>
<td>8.00</td>
<td>0.13</td>
<td>0.20</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Balance</td>
<td>10.00</td>
<td>0.15</td>
<td>0.26</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Balance</td>
<td>12.00</td>
<td>0.29</td>
<td>0.37</td>
<td>1.45</td>
</tr>
</tbody>
</table>

3.3 Test conditions

As already mentioned, the sintering temperature in the tests was 1123 K. From the phase diagram of the Cu–Sn system, the liquid phase starts to form into bronze containing 20 mass% Sn at approximately 1123 K; thus, SBP8, SBP10 and SBP12 undergo liquid-phase sintering. The mesh belt speed was set at 0.43 mm/s for the first sintering and at 0.33 mm/s for the second. Thus, the test specimens were maintained at the maximum temperature of 1113 K for 1050 s during the first sintering and for 1368 s during the second sintering. The sintering tests were conducted under reducing and inert atmospheres, as shown in Table 2. Some tests were conducted using a complex procedure in which the materials were sintered under inert gas during the first sintering and under reducing gas during the second (indicated as SB8c or SBP12c according to the notation in Table 2). Under the reducing atmosphere, not only oxygen but also sulphur might be reduced.

Table 2 Atmospheres used during sintering

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Sintering process*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First</td>
</tr>
<tr>
<td>a</td>
<td>Reducing</td>
</tr>
<tr>
<td>b</td>
<td>Inert</td>
</tr>
<tr>
<td>c</td>
<td>Inert</td>
</tr>
</tbody>
</table>

*Reducing atmosphere, H$_2$ (flow rate 5 L/min) and N$_2$ (85 L/min), inert atmosphere: N$_2$ (90 L/min)

Here, the reducing atmosphere was a mixture of hydrogen gas and nitrogen gas and the inert atmosphere consisted only of nitrogen gas. Hydrogen sulfide gas might have formed, resulting in a decrease in the concentration of sulphur in the Cu–Sn. Thus, sintering under an inert atmosphere was also performed to compare the states of sulphur and sulfide in the Cu–Sn. Between the first and second sinterings, a rolling process was performed by roll milling. The thickness of the bimetal was adjusted so that the entire surface of the Cu side of the bimetal was in contact with the roller surface.
4. Results and discussions
4.1 After first sintering

Fig. 2. Sectional view of sintered bimetal specimens after their first sintering under a reducing atmosphere. The bottom part of each image shows the steel.

Fig. 3. Surface and interface view of sintered bimetal specimens after their first sintering under a reducing atmosphere.

large pores and as-atomized state, with particles containing small dots of sulfides, were observed.
Figure 2 shows optical microscope images. The bottom part of each image shows the steel, to which the sintered Cu alloy adhered. In these images, all six specimens appear to be well sintered. However, some pores and as-particle states were observed, as shown in Fig. 3. In particular, SB8a with a low Sn content was sintered in a solid phase. Thus, open large pores and as-atomized state, with particles containing small dots of sulfides, were observed, as can be seen in Fig. 3(a) and 3(b). Concentrated sulfides (Cu–Fe–S) were also observed at the interface between the Cu alloy and the steel in Fig. 3b. These phenomena can also be seen with SB10a and SB12a. However, the pore sizes became smaller, as shown in Fig.

![Figure 4](image1)

**Figure 4.** Sectional view of sintered bimetal specimens after their first sintering under an inert atmosphere. All six specimens exhibited more pores than alloys sintered under a reducing atmosphere.

![Figure 5](image2)

**Figure 5.** Interface view of sintered bimetal specimens after their first sintering under an inert atmosphere. Under the reducing atmosphere, sulphur contained in the sulfides in the alloy was apparently reduced and converted into hydrogen sulfide gas in the furnace.
3(c) and 3(d). In addition, Cu–Sn compounds were only observed in SB12 (Fig. 3(d) and 3(e)). The compounds seemed to be Cu$_3$Sn from comparison with the results of previous work (Sato et al., 2010, 2011). On the other hand, effective diffusion apparently occurs via liquid-phase sintering for SBP8a, SBP10a and SBP12a in Cu–Sn, because Cu–20Sn powders begin to melt at 1071 K, which is below the sintering temperature of 1113 K used in this work. Figure 4 shows optical microscope images of the bimetal SB series and SBP series sintered under an inert atmosphere. All six specimens exhibited more pores than alloys sintered under a reducing atmosphere. In the sintered Cu–Sn, a dark-brown network apparently composed of sulfide was present to a greater extent than in the specimens treated under a reducing atmosphere, as can be seen in Fig. 5(d) and 5(e). Under the reducing atmosphere, sulphur contained in the sulfides in the alloy was apparently reduced and converted into hydrogen sulfide gas in the furnace. Cu$_3$Sn compounds were also observed in SBP12b (Fig. 5(e)).

4.2 After second sintering

4.2.1 Reduction atmosphere

Figure 6 shows the results for bimetals after their second sintering under a reducing atmosphere. The pores in the sintered copper alloy have almost disappeared. However, the alloy and steel have separated, as can be seen in Fig. 6(b), and the sulfides have almost disappeared from the copper alloy specimens. During the second sintering process, the copper alloy specimens were sintered to the extent that their pores disappeared. Figure 7 shows sectional views of the specimens after they were subjected to a second sintering under an inert atmosphere. Because of the rolling procedure performed between the first and second sintering cycles, all of the copper alloy specimens were well sintered and contained few pores. Sulfides remained in the specimens because the lack of a reducing atmosphere prevented the sulphur from reacting.

4.2.2 Complex atmosphere

Figure 8 shows sectional views of the sintered bimetal specimens after they had been subjected to a second sintering under a reducing atmosphere following a first sintering under an inert atmosphere. The copper alloy in all of the specimens was well sintered and contained fewer pores than the specimens sintered only under an inert atmosphere for both their first and second sintering cycles. However, the sulfide contents at the surface side and at the interface between

![Figure 6](image_url)

Figure 6. Sectional view of sintered bimetal specimens after their second sintering under a reducing atmosphere. The pores in the sintered copper alloy have almost disappeared.
the copper alloy and steel appeared to differ. Therefore, we analysed SPB10c using EDS and a simplified quantitative method. We observed that the sulphur at the surface side virtually disappeared, as shown in Fig. 9(a) and 9(b), with only 0.2 mass% S being detected by the simplified quantitative method. In contrast, the sulphur at the interface remained, as shown in Fig. 9(c) and 9(d), with 2.2 mass% S being detected. Thus, the second sintering under a reducing atmosphere

![Figure 7](image1.png)

Figure 7. Sectional view of sintered bimetal specimens after their second sintering under an inert atmosphere.

Because of the rolling procedure performed between the first and second sintering cycles, all of the copper alloy specimens were well sintered and contained few pores.

![Figure 8](image2.png)

Figure 8. Sectional view of sintered bimetal specimens after their second sintering under a reducing atmosphere.

These bimetals were sintered under an inert atmosphere in their first sintering.
resulted in the removal of sulphur from the surface of the copper alloy.

4.3 Hardness

The Vickers hardness values of the steel specimens and the sintered copper alloy are shown in Figs. 10 and 11. The average value of five points was shown the figures. As can be seen in Fig. 10, the hardnesses of the steels remained almost the same throughout the sintering and rolling process. For the steels, these thermal and working conditions did not change their microstructure or strength. It is important for bimetal bushings that the properties of the steel should remain constant.

From the results obtained here, it appears that the manufacturing conditions used are suitable for bimetals. As shown in Fig. 11, the results can be divided into three categories according to sintering atmosphere. For all of the test groups subjected to their first sintering, the alloys with high Sn content become harder. Cu–Sn alloys are known to become harder with increasing Sn content within the range of Sn content of the specimens investigated in this work. As a result, the basic properties of the Cu–Sn alloy in the sintered Cu alloys and the sulfide content of the Cu alloy had little influence on the hardness of the matrix. After the rolling process, some samples became harder, whereas others did not. The increase in hardness of some specimens might be a consequence of work hardening during rolling, and the lack of an increase in other specimens might have resulted from destruction of the interface formed by solid diffusion between the powders. A comparison of hardness between SB groups and SBP groups after the second sintering reveals that the SB groups became harder for each Sn content (i.e. 8, 10 and 12 mass% Sn) because Sn, as a solid solution in the matrix, can form intermetallic compositions such as Cu₃Sn after the second sintering in the case of the SBP series. In this series, liquid-phase sintering occurs during the first sintering.

![Figure 9 SEI images and Sulfur peak of SPB10c after second sintering.](image)

Only 0.2 mass% S being detected by the simplified quantitative method. In contrast, the sulphur at the interface remained, as shown in Fig. 9(c) and 9(d), with 2.2 mass% S being detected.

![Figure 10 Vickers hardness of steels under inert atmosphere.](image)

The hardnesses of the steels remained almost the same throughout the sintering and rolling process. For the steels, these thermal and working conditions did not change their microstructure or strength.
Figure 11. Vickers hardness of Cu matrix. For all of the test groups subjected to their first sintering, the alloys with high Sn content become harder. Cu–Sn alloys are known to become harder with increasing Sn content within the range of Sn content of the specimens investigated in this work. As a result, the basic properties of the Cu–Sn alloy in the sintered Cu alloys and the sulfide content of the Cu alloy had little influence on the hardness of the matrix.
under the experimental sintering conditions. As a result, a matrix that contains less Sn becomes softer after sintering. Moreover, specimens sintered only under an inert atmosphere (Fig. 11(b)) had hardnesses that were similar to or lower than those of specimens sintered only under a reducing atmosphere (Fig. 11(a)). A reducing atmosphere might accelerate the sintering process at the same sintering temperature. From these results, it appears that the use of pre-alloyed atomized bronze-containing sulfides does not result in poorer mechanical properties such as hardness. In Figure 12, relation between Vickers hardness of Cu matrix and the thickness for Inert (1st) and reducing (2nd) is shown. These two factor had correlation and the multiple correlation coefficient is 0.83. As a result, hardness is seemed to affect by thickness nevertheless thickness become smaller by the sintering or rolling.

5. Summary

By subjecting specimens of sulfide-dispersed bronze that had been water atomized to sintering, we observed the effects of sulphur or sulfide on the mechanical properties of bronze specimens sintered under reducing and inert gas atmospheres. Moreover, solid-state and liquid-phase sintering were compared for alloys with the same Sn content. As a result, we have drawn the following conclusions:
1. The use of pre-alloyed atomized bronze-containing sulfides does not lead to any significant decrease of hardness.
2. The Sn content affected hardness properties irrespective of whether the specimens were subjected to solid-state sintering or liquid-phase sintering; in contrast, the sulphur and sulfide contents of the specimens did not appear to influence hardness.
3. The sulfide content of the specimens decreased during sintering under a reducing atmosphere. However, the sulfide content did not affect the hardness of the copper alloy matrix.

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