Removal of Lead from Scrap Bronze*1

Atsushi Nakano1,2,3, Naoki Kajiya1,2, Kosaku Yamada2, Syun-ichi Nakamura3, Takehiko Matsuda3 and Hidekazu Sueyoshi1

1Graduate School of Science and Engineering, Kagoshima University, kagoshima 890-0065
2Kyushu Tabuchi Co., Ltd, Kokubu 899-4462
3Kagoshima Prefectural Industrial Technology, Aira-gun, Kagoshima 899-5105

Pb has been added to bronze to increase its machinability. However, due to the extreme toxicity of Pb that is harmful to the health, the public demand for the use of Pb-free bronze has increased. Therefore, scrap bronze containing Pb cannot be utilized as a recycling material and a large amount of scrap bronze will become industrial waste. So, it is necessary to remove Pb in the scrap bronze to promote recycling.

In the present study, the use of the compound-separation method is attempted for the removal of Pb from bronze containing 5.5 mass% Pb. The result shows that the percentage of Pb removal was effective up to 82% when NaF was added to molten bronze, followed by adding a Ca-Si alloy. [doi:10.2320/matertrans.47.2997]

(Received July 31, 2006; Accepted October 12, 2006; Published December 15, 2006)

Keywords: lead removal, lead-free bronze, recycle, compound-separation method

1. Introduction

In order to increase the machinability of bronze, several mass% of Pb was added to it. However, the leaching standard value of Pb was severely revised to 0.01 mg/L in Japan in April, 2003.1) In response to this, the development of Pb-free bronze has been advanced. However, a new problem such as resource consumption occurs because most of the developed Pb-free bronze is manufactured using virgin materials.

A new technology for removing Pb from bronze scrap has not been established. If we continue the manufacturing method only, using virgin materials, an enormous amount of bronze scrap containing Pb will be accumulated without being recycled. The evaporation method using Cl and oxidation method has been applied to remove Pb from bronze so far.2) However, these methods may not be applied today because of their large environmental impacts and long treating time.

In the previous study,3–5) the compound-separation method in which the floating Pb compound was skimmed off from the surface of molten brass was examined. However, this method may not be applied in the bronze because the composition and melting point are different from brass. The investigation of the new method for removing Pb from the scrap bronze containing Pb is required to promote scrap bronze recycling.

In the present study, removal of Pb from molten scrap bronze using the compound-separation method was investigated.

2. Experimental Procedure

Bronze (JIS CAC406) containing 5.5 mass% Pb was used as test specimens. Figure 1 shows the chemical composition of bronze. Table 1 shows the chemical composition of bronze.

Table 1 Chemical composition of CAC406 alloy used (mass%).

<table>
<thead>
<tr>
<th>Cu</th>
<th>Pb</th>
<th>Sn</th>
<th>P</th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>83.11</td>
<td>5.50</td>
<td>4.56</td>
<td>0.011</td>
<td>0.28</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>6.33</td>
</tr>
</tbody>
</table>

Fig. 1 SE image of as-received CAC406 alloy.

Fig. 1 SE image of as-received CAC406 alloy.
Gibbs energy ($\Delta G^\circ$) for synthesis of Ca$_2$Pb, Ca$_2$Sn and SnF$_4$ as function of temperature. $^6$ Sn reacts with Ca in preference to Pb; on the other hand, Sn reacts with F in preference to Ca. Therefore, NaF was added to the molten bronze to form the Sn-F compound, followed by adding the Ca-Si alloy. It may be expected that large solid Ca-Si-Pb compound become easier to move up to the surface of molten bronze.

Figure 3 shows a schematic illustration of the experimental procedure. Bronze was melted using high-frequency induction furnace (20 kW) under nitrogen gas atmosphere. Carbon crucible was used as melting pot (Inner diameter: 110 mm, high: 250 mm). Commercially Ca-Si alloy (Ca:28.8 mass%, Si:61.0 mass%, Al:1.48 mass%, Fe:5.1 mass%, C:0.64 mass%) was used as an addition agent. According to X-ray diffraction (XRD), this alloy consists of CaSi$_2$ and Si. In order to form Ca-Si-Pb compound, the Ca-Si alloy was added to the molten bronze at 1323 K after NaF addition. After agitating and holding, the formed large Pb compounds rose through the molten bronze. In the above-mentioned processes, the amount of the Ca-Si alloy and the Pb compounds removal temperature were changed. After casting into a metal mold, quantitative analysis of Pb in the specimens was carried out by X-ray fluorescence (XRF). The microstructures of both casting bronze and Pb compound which is formed in the molten bronze were characterized by EPMA.

### 3. Result and Discussion

Figure 4 shows the relationship between Pb removal and the amount of Ca-Si alloy (Pb compound removal temperature: 1183 K). The percentage of Pb removal increases with increasing the amount of Ca-Si alloy. However, it tends to saturate with further 10 mass% additions in bronze.

Figure 5 shows the relationship between Pb removal and Pb compound removal temperature (The amount of Ca-Si alloy: 8 mass%). The percentage of Pb removal increases with decreasing Pb compounds removal temperature. But, when Pb compounds removal temperature is lower than 1183 K, the percentage of Pb removal decreases.

Figure 6 shows EPMA analysis of the specimen before Pb compound removal (The amount of Ca-Si alloy: 8 mass%). The distribution of Pb is similar to that of Ca, that is, Ca-Pb compounds are formed. On the other hand, the distribution of Sn is not similar to that of Ca. This suggests that the reaction of Sn and Ca was disturbed by the addition of NaF. The Pb compound is very large (several ten $\mu$m) as shown SE images. Therefore, it is considered that
these large Pb compounds move up easily to the surface of molten bronze.

Figure 7 shows EPMA analysis of the specimen after Pb compound removal (The amount of Ca-Si alloy: 8 mass%, Pb compound removal temperature: 1183 K). The distribution of Pb is similar to that of Ca and Pb exists in the molten bronze as Ca-Pb compound (Ca\(_2\)Pb). However, these formed Ca-Pb compound is present as a small particle of several μm in size. This indicates that such small particles of a Pb compound can not be moved up to the surface of molten bronze, results in low percentage of Pb removal.

The above-mentioned results are considered based on equilibrium phase diagram of the Ca-Pb system. Figure 8 shows equilibrium phase diagram of the Ca-Pb system. It is assumed that every Ca-Si alloy reacts with Pb. When the 10 mass% Ca-Si alloy is added to molten bronze, Pb concentration in the Ca-Pb alloy becomes 65.6 mass%. According to equilibrium phase diagram, both liquid phase and solid phase (Ca\(_2\)Pb) coexist (Ca-Si alloy addition temperature: 1323 K). The ratio of liquid phase is larger than that of solid phase in bronze. After holding for a while under such a condition, it is considered that adjacent liquid phases coalesce to each other and grow up to a large liquid phase. When the temperature is lowered, the ratio of solid phase increases. In others words, more solid phase is crystallized in a liquid phase. Consequently, the amount of solid phase increases with the decrease in temperature. The percentage of Pb removal increases with decreasing the Pb compound removal temperature as shown in Fig. 5. This is because the Pb compound of solid phase grows up to large one owing to crystallization of solid phase in a liquid phase. It is considered that large particle of Pb compound having more solid phase becomes easier to move up to the surface of molten bronze. However, when Pb compounds removal temperature is lower than 1183 K, the percentage of Pb removal decreases (Fig. 5). This is because the Pb compounds of solid phase can not move up readily due to the high viscosity of molten bronze at near solidification temperature. As shown in Fig. 1, the percentage of Pb removal is 82% at 1183 K in Pb compound removal temperature. According to equilibrium phase diagram (Fig. 8), not only solid phase but also liquid phase exists at this temperature. This small liquid phase remains in molten bronze (Fig. 7), because it is not possible to skim off from the molten bronze.

The result of EPMA analysis of casting bronze after Pb removal process showed that Na was absent in casting bronze, but a small amount of Ca and Si remain in the casting bronze. However, residual Ca and Si in the molten bronze may be removed by oxidation refining. Thus, it is possible to recycle bronze scrap containing Pb using this new compound-separation method.
The compound-separation method for removing Pb from bronze containing 5.5 mass% Pb was investigated. NaF was added to the molten bronze to form Sn-F compound, followed by adding Ca-Si alloy to the molten bronze. Therefore, the reaction of Ca with Pb is promoted without the reaction of Ca with Sn. The formed large particles of Pb compound moves up easily to the surface of molten bronze, resulting in the high percentage of Pb removal. In this method, the percentage of Pb removal changes by the amount of Ca-Si alloy and Pb compound removal temperature. In the present study, 82% of Pb can be removed from bronze containing 5.5 mass% Pb.

**Acknowledgments**

This work was supported by a Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science, No. 16510063.

**REFERENCES**

6) HSC chemistry 5.0: Outokumpu Research.