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Pb-Free Brass from Scrap by Compound-Separation Method

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In the near future, a huge amount of scrap brass containing Pb will become industrial waste because a new regulation to limit the amount of Pb permitted in drinking water supplies has been enforced. As an alternative to recycle scrap brass, the compound-separation method for removing Pb from brass has been developed in the present study. Brass containing 2.15 mass % Pb was melted at 930°C by using a high-frequency induction furnace under nitrogen atmosphere. Calcium-silicon (Ca-Si) compound was then added into the molten brass so that it reacted with Pb to form Pb-Ca-Si -like compound. After skimming off this compound, a flux that mainly composes of NaF, was also added to remove the remained Pb, Ca and Si from molten brass. After the NaF flux addition, the big compound, which composes of Pb, Ca, Si, Na and F, was formed and floated to the surface of the molten brass so that it made easy to be skimmed off using an agitation rod. After casting into a metal mold, the ingot was characterized by EPMA and fluorescence X-ray (XRF) analysis. The result shows that 83 % Pb removal can be achieved. Therefore Pb-free brass can be obtained from scrap brass and at the same time environmental problem also can be solved. Thus, the Pb-free brass obtained in the present study can be considered as an ecomaterial.

Key words: Pb-free brass, compound-separation method, Pb removal, aggregation agent, ecomaterial

1. INTRODUCTION

Pb was added into brass to increase the machinability. However, due to the adverse toxicity of Pb that is harmful to the health, the public demand to use Pb-free brass, especially in water supplies, becomes increase. Now, the regulations to limit the amount of Pb permitted in drinking water supplies are enforced. Japan reduced Pb limit standard from 0.05 mg/L to 0.01 mg/L. In the future, it will be 0.005 mg/ L. As a countermeasure, the development of Pb-free brasses made from pure Cu, Zn and other alternative elements to Pb has been done [1,2]. However, many problems have arisen during implementation, such as high cost and depletion of resources. Furthermore, because the current scrap brass containing Pb will be unable to be recycled, a huge amount of scrap brass will become industrial waste.

Therefore, to meet the demand for using Pb-free brass and to avoid the high cost and depletion of the resources, the method of removing Pb from scrap brass is suitable. As the methods for Pb removal, so far conventional gas bubbling and oxidation methods have been attempted [3,4]. Kobe Steel Company [5,6] has developed a compound-separation via filter method, by adding Ca in molten brass, so that Ca reacts with Pb to form $PbCa_2$ compound. This compound was separated using a pressurized filter. Nevertheless, the percentage of Pb removal was low (29%) because the grain size of the compounds was very small (several μm).

Therefore, the above-mentioned methods may not be applied today due to high cost, environmental pollution etc. It is expected to develop a technology with low cost, small burden to environment and applicable to industry. If large Pb compound can be made so that it floats to the surface of the molten brass due to the lighter specific gravity, compared to that of brass, the separation of Pb compound from the molten brass becomes easy. In the previous study[7], the possibility of Pb removal by this compound-separation method was confirmed. By optimization, the Pb removal percentage is about 55 %[8]. In order to increase the Pb removal percentage, several fluxes were considered.

Therefore in the present study, the compound-separation method to remove Pb by adding Ca-Si compound followed by adding a flux containing NaF was investigated.

2. EXPERIMANTAL PROCEDURE

Figure 1 shows the schematic illustration of the experimental procedure. Brass (5 kg) containing 2.15 mass % Pb (JIS (Japan International Standard): CAC203) was melted at 930°C by using a high-frequency induction furnace under nitrogen atmosphere. After entirely melted, the temperature was set to a certain processing temperature (900°C). In order to separate Pb from molten brass, Ca-Si compound (200 g), which mainly composes of $CaSi_2$ was added into the molten brass so that it reacted with Pb to form Pb compound. After agitation and holding for a certain time, this Pb compound floated to the surface of the molten brass. The compound was then skimmed off from the molten brass by using an agitation rod. In order to remove the remained Pb, Ca and Si, a flux, which mainly composed of NaF was added into the molten brass. After agitation and holding a certain time, the floated compound was skimmed off and then the molten brass was poured into a metal mold. The specimen from the ingot was characterized by EPMA and fluorescence X-ray (XRF) analysis.

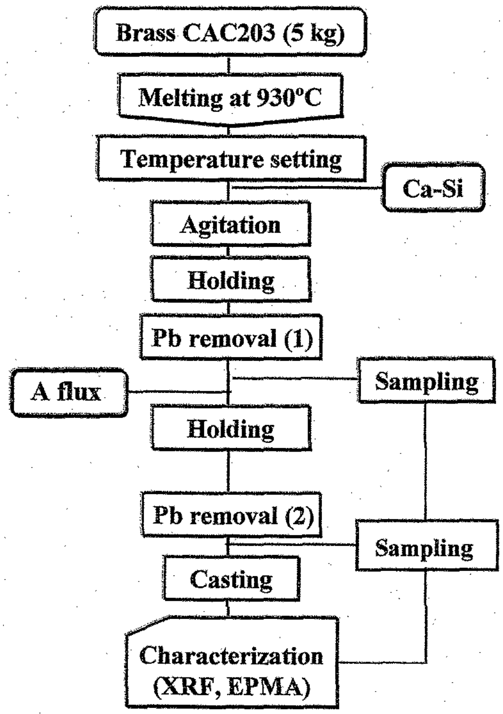

Figure 1 Schematic illustration of experimental procedure.

3. RESULT AND DISCUSSION

Figure 2 shows EPMA analysis of as-received brass CAC203 containing 2.15 mass % Pb. The color change from black to white indicates that the intensity of element content changes from low to high. Therefore, the white area in SEM image is considered to be Pb grain. As shown, many Pb grains are dispersed in the matrix of brass before Pb removal.

As reported previously, by adding Ca-Si compound into the molten brass, so that it reacted with Pb to form Pb-Ca-Si -like compound. When this compound was skimmed off, about 55 % of Pb removal percentage could be achieved[8]. Figure 3 shows EPMA analysis of brass after Pb removal by using Ca-Si compound. As shown, despite of Ca-Si compound that is dissolved in the matrix, several Pb with grain size smaller than 10 μm still remains. It is considered that if the processing temperature is high or the holding time is too long, Ca-Si compound is easy to liquefy and finally it is dissolved in the matrix of the brass. Therefore, this may give a bad effect on the mechanical properties of brass itself.

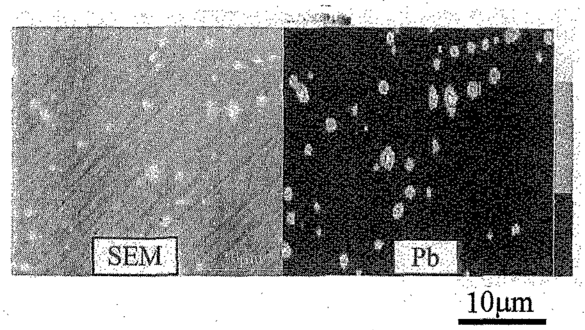

Figure 2 EPMA analysis of as-received brass CAC203 containing 2.15 mass % Pb.

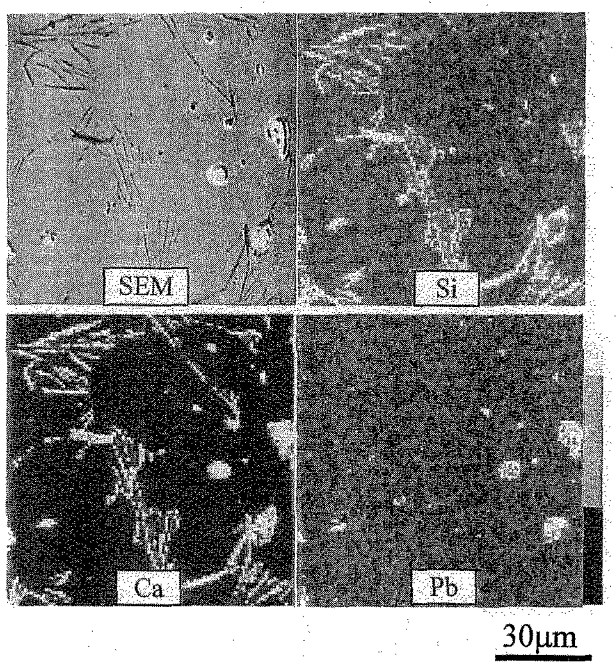

Figure 3 EPMA analysis of brass after Pb removal by using Ca-Si compound.

In order to remove the remained Ca-Si and Pb compound, a flux is considered to be as an alternative. First, the most possible elements that are able to react with Pb, Si and Ca are selected based on the Gibbs standard free energy change (ΔG°) calculated using HSC Chemistry 5 software (Outokumpu Research). Figure 4 shows ΔG° as a function of temperature. It is found that the NaF is the most desirable flux. The ΔG° of Si_2F_6 and SiF_4 are not plotted in Figure 4 because they are very large, about -1886 and -40729 kJ/mol at 1000°C respectively. It means that Si and F will react faster than other components. Also, ΔG° of NaF is much larger than those of the compounds formed from Pb, Si, Ca such as CaSi, CaPb etc. While, ΔG° of PbF_4, PbF_2 and CaF_2 are larger than that of NaF. Therefore, it is assumed that F from NaF will react with Pb, Si and Ca, and the formed Pb-Ca-Si -like compound will float to the surface of the molten brass due to the lighter specific gravity.

Figure 5 shows the result of Pb removals after additions of Ca-Si compound and NaF flux. When only Ca-Si compound is used, 43 % Pb content can be removed. This is because; compound-separation by Ca-Si addition only has a limitation as mentioned previously. However, with NaF flux addition, Pb removal percentage increases significantly up to 83 %. Figure 6 shows EPMA analysis of the brass after Pb removal through compound-separation by both Ca-Si compound and NaF flux. As shown, no remained compounds from Ca, Si and Pb elements are observed except several small Ca-Pb compounds. This indicates that almost the remained Ca, Si and Pb, which are shown in Figure 3 react with NaF, and the formed compounds float to the surface of the molten brass, so that it makes easy to be skimmed off. Figure 7 shows EPMA analysis

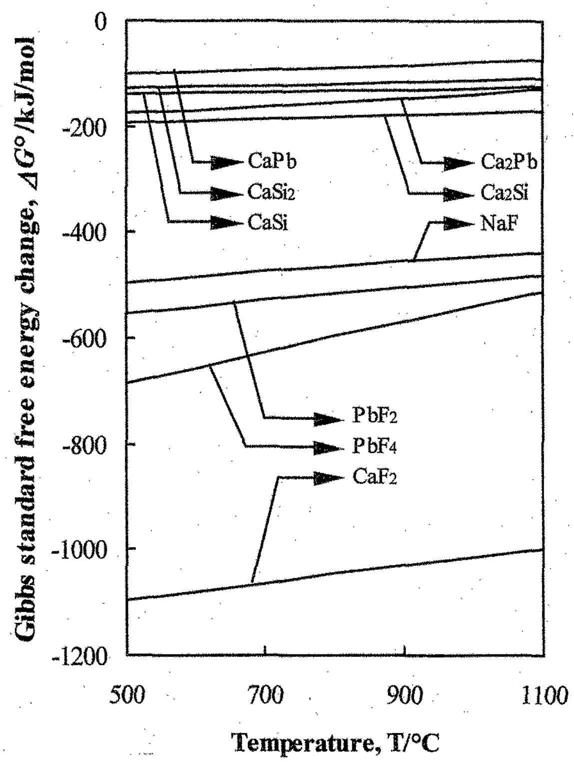

Figure 4 Gibbs standard free energy change as a function of temperature.

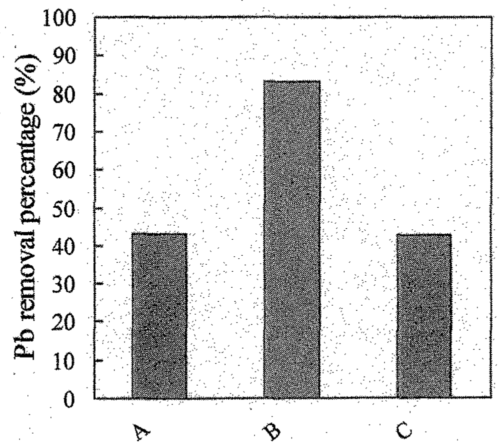

Figure 5 Result of Pb removals. *A: Ca-Si compound, B: Ca-Si compound + NaF flux, C: NaF flux.*

of the cross section of the skimmed off materials. As shown, a big compound, which composes of Pb, Ca, Si, Na and F, is observed. Therefore, this big compound is able to float to the surface of the molten brass because of its light specific gravity and easy to be separated from the molten brass. Thus, the high Pb removal can be obtained as shown in Figure 5.

On the other hand, when only NaF flux is used, Pb removal is as low as that by Ca-Si compound addition, about 42.8 %. Figure 8 shows EPMA analysis of the brass after Pb removal through compound-separation by NaF flux only. Many small Pb compounds, which mainly compose of Pb and F less than 5 μm in the size are observed. Since the size of the formed compound is very small, they cannot float to the surface of the molten brass and are remained in the brass. It is considered that only the larger Pb-Na-F compounds floats so that can be separated from the molten brass.

Based on the above results, the most effective way to obtain the highest Pb removal percentage is by compound-separation through additions of both Ca-Si compound and NaF flux. When 83 % Pb content can be removed from the brass (CAC203), it is considered that the leaching Pb from the brass obtained in the present study is under 0.01 mg/L. So that this will satisfy the Pb limit standard regulation. By using this method, the huge scrap brasses can be recycled and high cost and environmental pollution can be avoided.

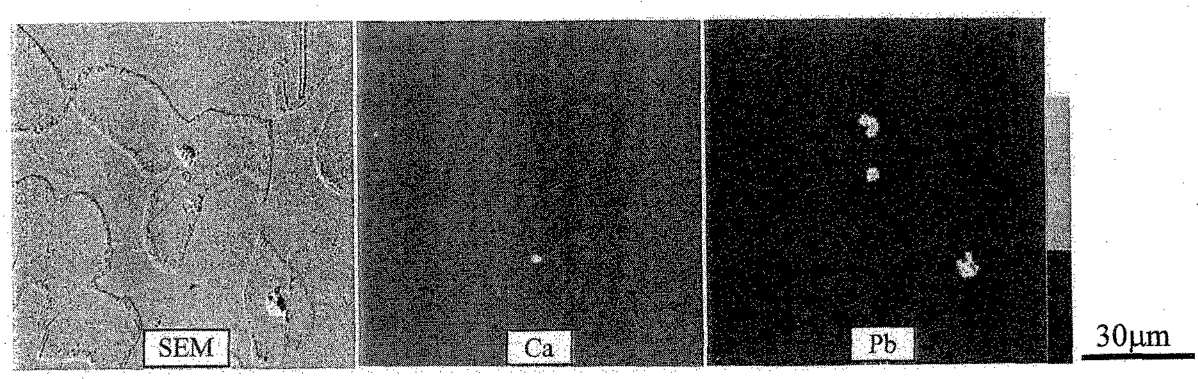

Figure 6 EPMA analysis of brass after Pb removal through compound-separation by both Ca-Si compound and NaF flux.

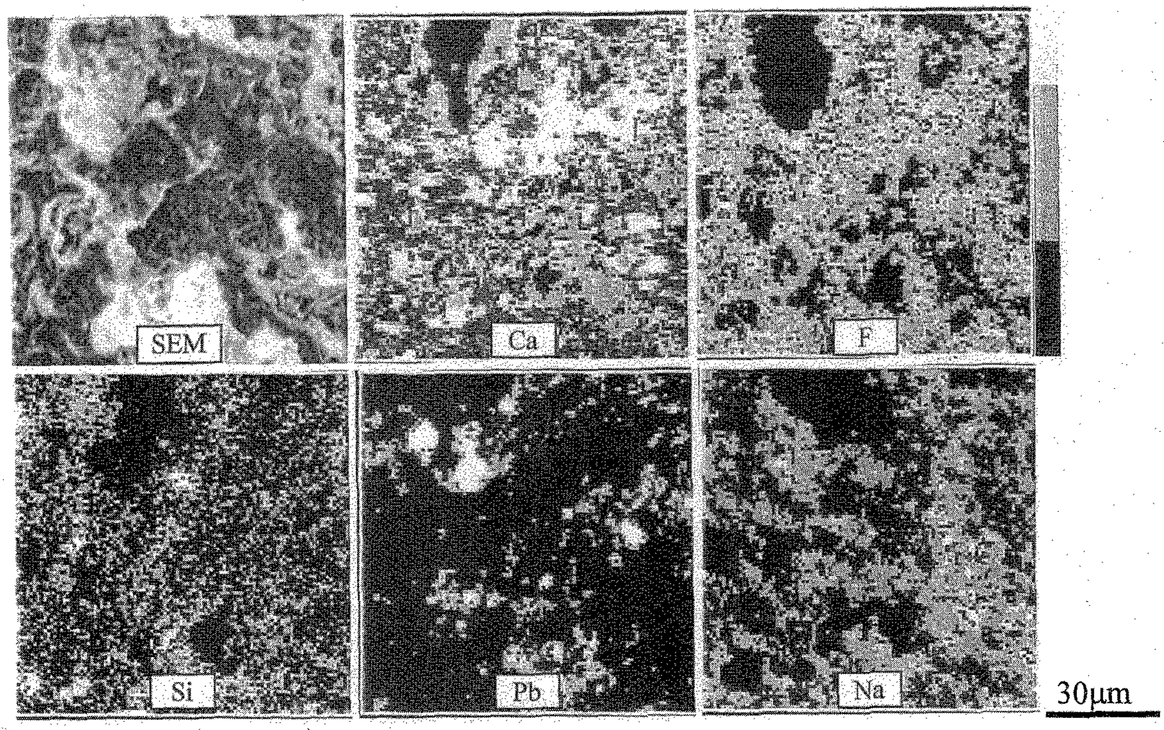

Figure 7 EPMA analysis of the cross section of the skimmed off materials.

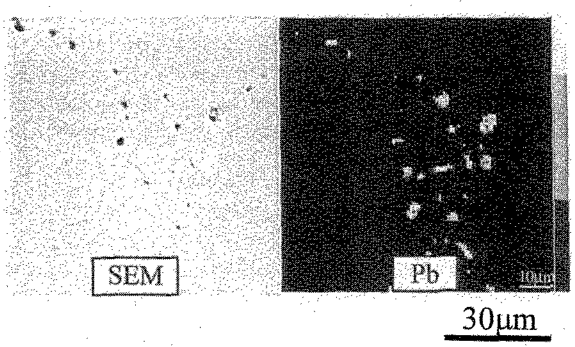

Figure 8 EPMA analysis of the brass after Pb removal through compound-separation by NaF flux only.

4. CONCLUSIONS

(1) In compound-separation method, when only Ca-Si compound is used to separate Pb from the molten brass, Pb removal has a limitation (near 43 %).

(2) When only NaF flux is used, many small Pb-Na-F compounds are remained in the brass. Therefore, Pb removal also has a limitation.

(3) When both Ca-Si compound and NaF flux are used, the highest Pb removal (83 %) is obtained. Thus, by using this method, the huge scrap brasses can be recycled and high cost and environmental pollution can be avoided. Therefore, the Pb-free brass obtained in the present study can be considered as an ecomaterial.

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