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A new approach for copper alloy recycling -Development of alloy to alloy process-

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Cu is one of the most popular non-ferrous metal used in a wide range of applications such as most electric appliances and automobiles. Thus the recycling of Cu baring material is important not only from the point of resource security but also waste minimizing. Most of in house waste or scrap is recycled by simple resmelting process. However, Cu scrap including rather high amount of impurities is treated by conventional smelting processes. Basically they are energy intensive processes and each metal as Cu and Zn can't be recovered by single process. That means a new eco-recycling process is necessary. Thus new hydro metallurgical approach has been examined to recover Cu and Zn by single process making Cu-Zn alloy deposition. For the basic research of the new process, alloy deposition test by means of electro chemical process in pyrophosphoric acid solution was carried out. In the report a new recycling process for Cu-Zn alloy is discussed.

1. Introduction

Cu consumption in Japan is about 3 million t/y. Most of them are used for wires and rolled materials as shown in Fig. 1. In Japan the almost all row materials of Cu are imported, thus from the point of mineral security, the recycling of Cu baring scraps becomes important issue. And also from the point of waste minimizing, a development of new process for Cu recycling is necessary as well. The authors have being studied the new recycling process[1,2,3], alloy to alloy process, in these years financially supported by Japanese Agency of Science and Technology. In this report the results of our basic investigations are discussed.

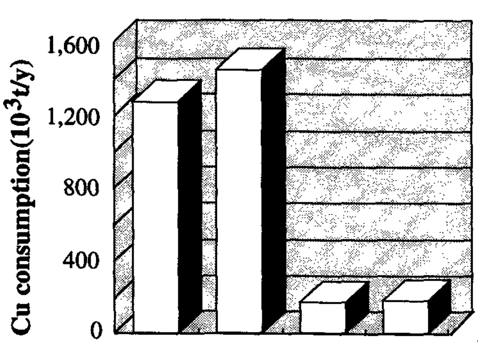

Fig.1 Cu Consumption in Japan [4]

2. Material flow of Cu in Japan

Fig.2 shows the material flow of Cu in Japan[5]. 1.5 million tons of Cu metal are produced by conventional Cu smelters from Cu concentrates. 1.2 million tons of secondary materials are treated by processing plants such as wire and rolling plants. Thus it can be said that the recycling ratio of raw materials is almost 30-40 %. However 340 thousand tons of Cu are missing as low grade Cu waste.

Cu and Cu alloy scrap which come from rolling and wire process or rather high purity scrap are treated by simple remelting process for raw material. Low grade scrap or scrap including rather high amount of impurities are treated by conventional smelting process and some of them are directly land filled. The conventional smelting process is energy conscious, it means high lords on the environment in various manners. Also conventional smelting process is designed for treating concentrate, thus it has a limit of the amount of impurities which can be processed. Thus, new recycling process for low grade Cu baring scrap to establish the sustainable development is essential. The authors are studying to develop a new process for recycling of low grade Cu scrap

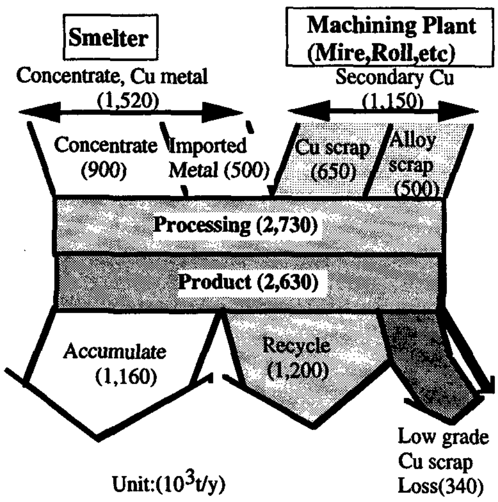

Fig.2 Material flow of Cu in Japan

by hydro metallurgical method which utilizing alloy deposition. This process caused lower environmental lords to the earth than conventional smelting process and also it is possible to recover Cu and Zn as alloy. So we can say this process is alloy to alloy process which raw material is alloy (scrap) and the product is also alloy.

3. The concept of alloy to alloy process

Fig.3 shows the concept of our alloy to alloy process. Right now the conventional Cu and Zn smelters are producing high grade metals from concentrate. At the mine site concentrate is being produced with destroying environmental condition with some extent. The concentrate is transported to Japan and treated at the conventional smelters. Produced high purity Cu and Zn are melted to Cu-Zn alloy such as brass. Then they are processed at rolling and machining plant to make parts for electronics appliances, auto mobiles and many other applications which are very important for our living. After the life of such many kinds of applications, they are discarded and forming a urban mine. The typical resources from urban mine is waste from car shredding process. It includes rather high amount of Cu and Zn and many kinds of impurities.

Table 1 shows a typical composition of car shredding scrap after separating the iron scrap. The main elements are Cu and Zn. Fe, Pb, Ni and Cr are also included as impurity elements. And this nonferrous metal scrap is treated by conventional smelting process or discarded by land filling. Thus by using this Cu and Zn bearing alloy scrap, we intend to develop a new recycling system to recover high purity Cu-Zn alloy by hydro metallurgical process. And these alloys can be used as virgin alloys made from conventional smelting process. This process could maintain a closed circuit for Cu metal consumption.

Table 1 Chemical composition of car shredding scrap

No.	Cu	Zn	Fe	Pb	Ni	Cr
(1)	48.3	31.6	6.99	2.84	0.85	-
(2)	49.1	35.7	-	3.59	0.36	0.17
(3)	55.8	30.6	-	-	0.31	0.49

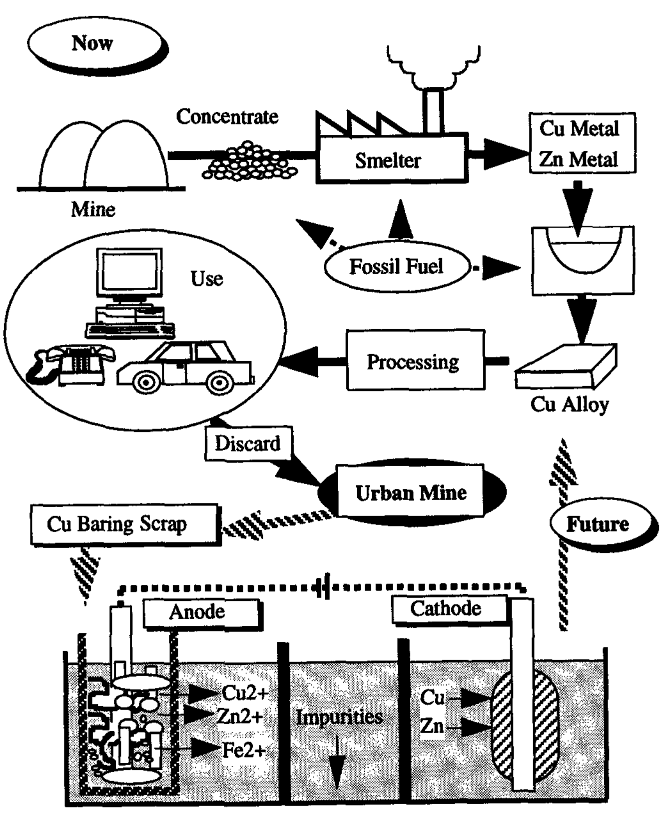

Fig.3 The concept of alloy to alloy process

4. Experiments and Result

4.1 Cathodic Paralyzation

The cathodic paralyzation tests were carried out to examine the possibility of the Cu and Zn alloy deposition. Sulfuric acid and pyrophosphoric acid are used as electrolyte. Pt and Al were installed as anode and cathode plate respectively. The typical result is shown in fig.4. In the sulfuric acid, the difference of cathodic potential (ΔE_1) is about 800 mV when the current density is approximately 10^4 μA/cm^2. It means that the Cu-Zn alloy deposition is difficult in sulfuric acid solution. On the other hand, in pyrophosphoric acid the polarization curves of Cu and Zn moved to less noble side and their difference at same current density (ΔE_2) becomes much smaller. It is about 200 - 300 mV and it means that the Cu-Zn alloy deposition might be possible. This change of cathodic potential difference woul be based on the formation of Cu and Zn complex ions in pyrophosphoric acid.

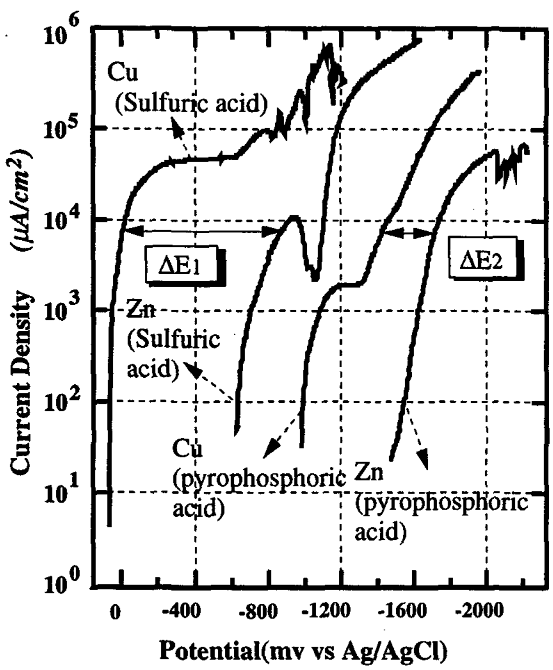

Fig.4 Cathodic paralyzation test

4.2 Alloy deposition test

Based on the results of cathodic paralyzation tests, the electrolytic alloy deposition tests under constant potential were done in pyrophosphoric acid. The pyrophosphoric acid concentrate is 1mol/l, Cu sulfate concentrate is 0.08 mol/l and Zn sulfate concentrate is 0.15 mol/l. The temperature of electrolyte is 30 °C . The result is shown in fig.5. As the potential becomes less noble the Zn concentrate in deposited alloy becomes higher.

At -1.2V the Zn concentrate in deposited alloy was 10%, at -1.4 it is 55% and at -1.6 V it became 60%. This results means that if the potential is controlled at certain value, the alloy composition can be controlled.

Zn concentrate in deposited alloy is higher without stirring than with stirring. This tendency is more clear at less noble potential. This phenomena seemed to be caused by the difference of metal ion transportation, and more detail study would be necessary.

The current efficiency is almost 90% independent on the cathodic potential. No apparent difference can be observed on influence of stirring. The typical result is shown in fig.6.

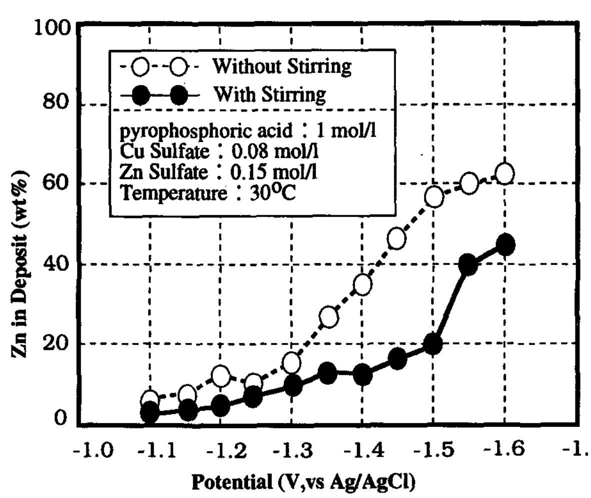

Fig.5 Relationship of Zn in deposit and potential

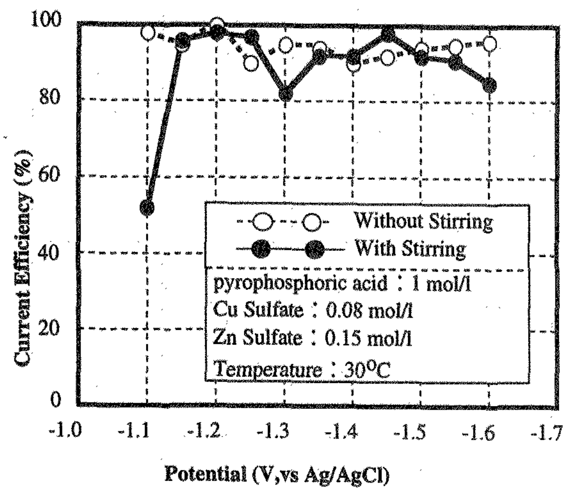

Fig.6 Relationship of current efficiency and potential

4.3 Surface condition of deposited alloy

The results of alloy deposition tests gave the possibility of Cu-Zn alloy deposition in pyrophosphoric acid. The surface condition of the deposited alloy is important for actual recycling process. Thus observation of the surface by scanning electron microscope (SEM) was done. Fig.7 shows the SEM image of the surface of deposited alloys. The morphology was changed by cathodic potential. At the cathode potential of -1.2V when the Zn contents is 4.84wt% the surface is rather flat and no dendrite was observed (A) . At the cathode potential of -1.4V when the Zn content is 23.80 wt%, some dendritic crystals wrer observed (B) . And at the potential of -1.6V when the Zn concentrate is 41.51 wt% larger dendritic crystal growth could be observed (C). These change of surface morphology was caused by the current density.

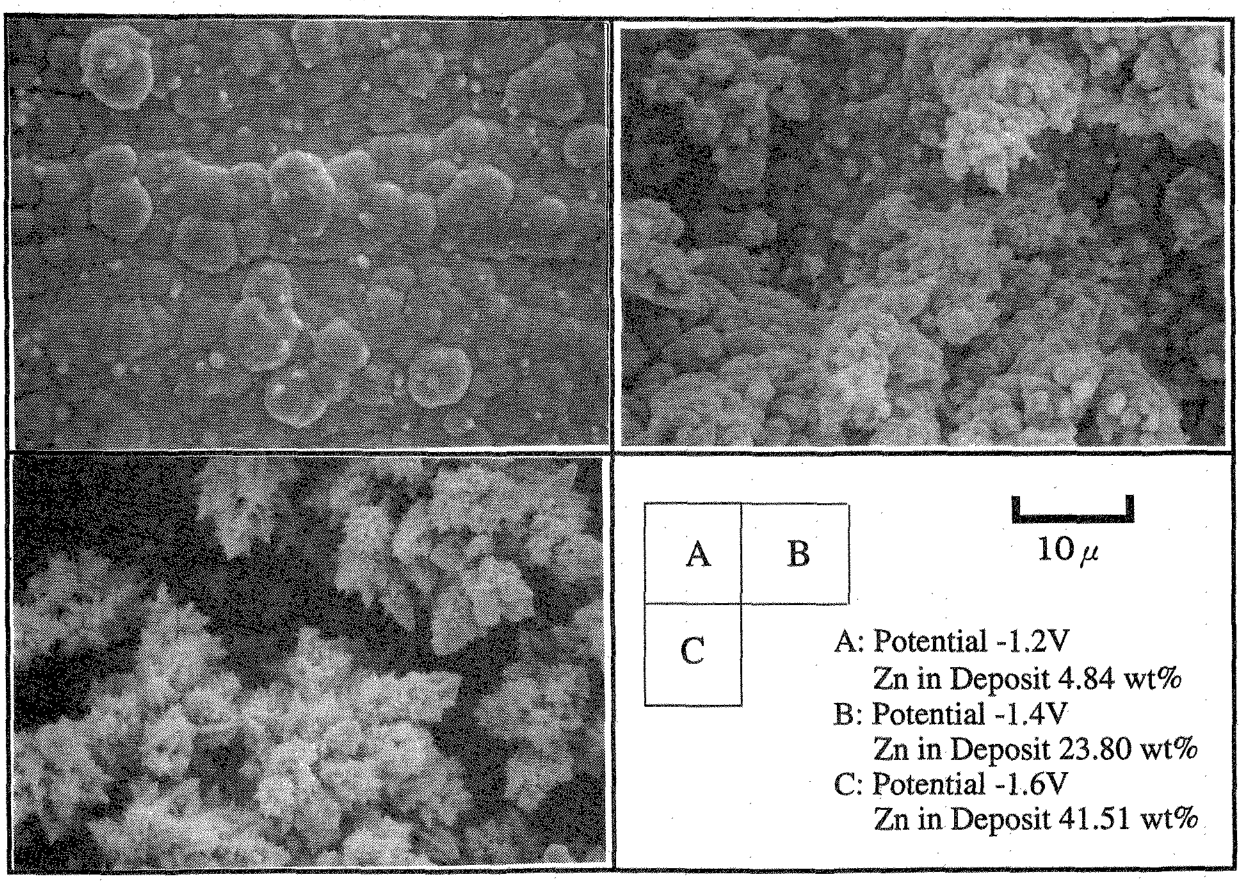

Fig.7 SEM image of deposited alloy

When the cathodic potential is rather noble, mass transfer of metal ions to the deposit surface is sufficient. However at less noble potential the mass transfer becomes insufficient, thus the deposit growth becomes more dendritic resulting very rough surface morphology. The control of the surface condition should be further considered to realize the alloy to alloy process.

5. Summary

Electro chemical research works have been done to develop a new recycling system , alloy to alloy process. Through the fundamental study following results were obtained.

(1) Alloy deposition of Cu and Zn in pyrophosphoric acid is possible.

(2) The chemical composition of deposited alloy depends on the cathodic potential , that is, as the potential becomes less noble the Zn content in the deposit increases.

(3) The current efficiency is rather high through in the certain range of cathodic potential.

(4) The surface morphologies drastically change by cathodic potential. At less noble cathodic potential the surface shows dendritic crystal grouth. Authers will continue the further investigation to realize the alloy to alloy process.

The further investigation will include the influence of impurity elements on electro deposition and elimination of major impurity elements. The improvement of the surface morphology will be studied as well.

Acknowledgements

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