A Study on the Recovery of Pb-Sn Alloy from Spent Photovoltaic Ribbons

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Abstract

This study aimed to develop a process that collects copper by thermally separating coating layers from copper ribbon electrodes in an anaerobic environment. Coating layers of copper ribbon electrodes were produced from an alloy of lead and tin that was easily melted and separated thermodynamically at a temperature of 300°C or higher. For the thermal process of coating layers of lead and tin without oxidation, the reactor environment should be kept anaerobic. An oxygen partial pressure of 10-70 atm was maintained by reacting argon gas with magnesium in advance for this environment. While maintaining the thermal process temperature at 800°C, copper of 9.5 wt. % was collected by separation from the alloy coating layers.

Keywords: Coating Layer, Copper Ribbon, Lead, Tin

1. Introduction

Previous Green energy sources are being studied and used in practice today due to fossil fuel depletion and global warming by the existing fossil energy industry. The practice and commercialization of solar energy, the greatest proportion of energy studies, are already in progress. According to McKinsey’s Global Solar Market Report (Solar Power: Darkest Before Dawn), the world’s accumulated installation capacity for solar power generation is expected to reach 400-600W in 2020. In Korea, solar generators of 680,000 KW are installed and operated as of 2010, and their number is gradually increasing². PV modules can be classified into the crystal type that was distributed before 2009 and the thin film type that has been distributed since 2009. The expected lifespan of a product manufactured before 2000 is 10 years. The expected lifespan of a product produced in 2001-2010 is 15 years. The expected lifespan of a product made after 2011 is 20 years. The number of solar power generation installations is shown to be rapidly increasing since 2008. Given the differences in expected lifespans of products made before and after 2010, it is forecast that processing waste PV modules will be become important starting in 2020. Waste due to damage during installation, fires and natural disasters should be considered. According to the PV Cycles report, only 1% of installed PV modules are used for their maximum lifespan.

Most metals used in PV modules depend on imports from overseas, and demand following the development...
policy of new renewable energy is increasing. The development of technology to collect valuable metals from waste PV modules leads to an import replacement effect due to source material security, and is anticipated that collected resources are recycled and supplied to PV modules.

A PV module is composed of the following components:

Figure 2. The composition of a PV module.

The composition includes glass that allows light to penetrate the top of the module to enter crystal silicon PV cells, cover glass, crystal silicon PV cells, EVA sheets that envelop material in contact with the back sheet, PV ribbons that act as passages delivering the electric energy produced by the crystal silicon PV cells, back sheets that protect the module from external air, shock, moisture and others at the rear of cover glass, and frames holding these components together.

No system that reuses waste PV modules is installed in Korea; waste PV modules are buried or neglected. Studies on technologies to select and disassemble modules and to collect wafers and glasses have been conducted by Korea Institute of Energy Research teams. Studies to collect high-purity copper by using hydrogen gas as the reducing agent, unlike methods which use atmospheric oxidation to separate the Pb-Sn layer, have been performed for the PV ribbon.

2. Materials

Figure 3 shows the PV ribbon structure currently in commercial use. Copper electrode is installed in the PV ribbon while Pb-Sn is uniformly coated on the exterior. The width is 1-4 mm while the thickness is 0.1-0.25 mm. The coating layer is composed of 64% Sn and 36% Pb with a small amount of Ag added. KOSBON PVC ribbon was used for this study. The analysis results are shown in the figures. The ribbon formed as copper positioned at the center of the PV ribbon and wrapped in a coating layer of 30 μm thickness. The figure shows the ICP analysis of the commercial PV ribbon. It contained 87.75% copper, 5.25% lead, and 6.15% tin with small amounts of Nb and Ag.

Figure 3. PV ribbon structure.

Figure 2.2 is a schematic drawing of the device to collect high-purity copper by reductive dissolution of the selected PV ribbon's coating layer. Ultra high-purity argon gas was injected during the experiment to prevent oxidation of the coating layer during the thermal process.

Materials were arranged so as to pass drierite (CaSO₄) to remove moisture contained in the argon gas. Later, the gas passed through the electric furnace containing magnesium chips through the gas meter. This arrangement minimized oxygen content that would be included even in ultra high-purity argon gas by reacting the oxygen with the magnesium.

Figure 4. Experimental apparatus of thermal reaction.

The following reaction formula shows the oxidation reaction of magnesium and oxygen at 500°C.

$$2\text{Mg(s)} + \text{O}_2(g) = 2\text{MgO(s)} \quad \text{P}_2 \text{O}_5 = 10^{-70} \text{ atm}$$
When this reaction was the condition for the equilibrium reaction, the partial pressure of oxygen in the argon gas was approximately $10^{-70}$ atm so that almost no oxygen content could be assumed. The argon gas through this reaction was injected into the reactor during the thermally processed reaction so that an inert condition was maintained.

Figure 5 shows the schematic drawing of the electric furnace used for this study. An SIC heating element is used as the heater and the reactor was produced by using SUS 310S. A stand was installed in the reactor to hold PV ribbons and an alumina crucible was installed at the bottom to collect the reduced and melted Pb-Sn. An O-ring was installed between the reactor and its cover to prevent internal gas leaks. The thermocouple was installed at the center of the reactor and the experiment was performed. The temperature was raised by 5°C / min to 800°C and maintained for 5 hours. During the temperature raising, $\text{H}_2$ gas (100cc/min) was injected while $\text{Ar}$ gas (100cc/min) was maintained.

![Figure 5. Schematic drawing of electric furnace.](image)

(a: Electric Furnace, b: PV Ribbons, c: Thermocouple, d: SIC Heaters, e: Alumina Crucible)

In this scheme, the melting points of Pb and Sn composing the coating layer of the PV ribbon were lower than that of Cu so that the coating layer materials were selectively collected before the collection of internal copper. However, the melting point of copper is 1,080°C, so the copper was collected in its original metal state.

### 3. Result and Discussion

The separation of coating layer of copper ribbon was conducted on the effect of temperature and time under reductive environment. The temperature should be over 300°C because eutectic temperature of lead and tin at given chemical composition. In order to find suitable temperature and time, several tests were carried out on the temperature range of 300°C to 900°C as well as 1 to 5 hours of reactive time.

The thermal process was conducted for 5 hours in an 800°C hydrogen environment to collect copper from PV ribbons in waste PV modules. As the figure shows, Cu and Pb-Sn were separated. Fig. 6 shows two specimen that is copper substrate (a) and coating layer (b) melted down after thermal treatment. The PV electrodes after coating layers were removed. Most Pb-Sn coating layers, except partial layers that had melted, yet not dropped down, were removed. ICP-OES(Inductively Coupled Plasma Optical Emission Spectrometry) analysis results show 99.554% copper and remaining coating layers. The coating layer made of lead and tin was successfully achieved and it was also analyzed by ICP. It is found that its alloy was composed of 68.21 wt.% of copper, 17.72 wt.% of tin and 10.91 wt.% of lead, respectively. Unfortunately, copper was also contained to the alloy and further study will be therefore done to reduce copper content in the alloy.

![Figure 6. Analysis results of collected Pb-Sn and Cu analyzed by ICP.](image)

Figure 7 shows weight change after experiment with copper substrate (a) and coating layer (b) and the analysis result of Pb-Sn dropped to the bottom. It is assumed that the Cu dropped as well. The reduction of Cu content is
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considered to be possible by controlling the temperature and time. When PV ribbons of 20 g were thermally processed, the weight of top copper electrodes was 15.1449 g and the weight of collected Pb and Sn at the bottom was 3.0391 g. Wight loss was found to be 1.2586 g and it can be expected that coating layer was dispersed on the bottom and/or trapped the screen between copper ribbon and it alloy in the reactor.

Figure 7. Weight change of two specimen after thermal treatment.

4. Conclusion

This study aimed to collect Cu, Pb and Sn from PV ribbons separated from waste PV modules. Cu base material and Pb-Sn coating layer were separated by a thermal process for 5 hours in a 800°C hydrogen environment. Cu of 99.554 wt.% (2N) was collected, and it was confirmed that 15.1449 g of Cu electrodes could be collected by processing 20 g.

5. Acknowledgment

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