廢太陽電池용 솔라리본으로부터 구리회收到 關한 研究

李鎮石 · 張普允 · 金僑秀 · 安永洙 · 姜埈煥 · *王帝弼*

韓國Energy技術研究院, Energy融合素材研究團, 太陽Energy研究團
*國立釜慶大學校 金屬工學科

Recovery of Copper from Spent Photovoltaic Ribbon in Solar Module

Jin-Seok Lee, Bo-Yun Jang, Joon-Soo Kim, Young-Soo Ahn, Gi-Hwan Kang and *Jei-Pil Wang*

Energy Materials and Convergence Research Department, Korea Institute of Energy Research, Daejeon 305-343, Korea

**Department of Metallurgical Engineering, Pukyong National University, Busan 608-739, Korea*

요 약

폐 태양광 전지내의 구리리본전극으로부터 구리를 회수하기 위해 불활성 가스분위기하에서 300-600°C로 열처리 하였다. 구리리본전극의 코팅층은 68.99 wt.%의 납과 31.21 wt.%의 주석으로 구성되어 있는데, 각각의 온도에서 코팅층을 용해한 후 반응도가나에 용해된 코팅층 회수하였다. 열처리 후 회수되어진 코팅층은 ICP-MS (Inductively coupled plasma mass spectrometry)로 성분 분석을 실시하였으며, 온도범위에 관계없이 95 wt.% 이상의 구리순도를 얻을 수 있었다. 구리리본전극 샘플의 횡단면은 SEM (scanning electron microscopy) and EDX (energy dispersive X-ray microscopy)로 관찰하였다.

주제어 : 구리, 구리리본전극, 열처리, ICP-MS

Abstract

The recovery of copper from spent photovoltaic ribbon was conducted using thermal treatment method at the range of temperature of 300°C to 600°C under inert atmosphere. The coating layer consisted of lead of 68.99 wt.% and tin of 31.21 wt.% was melted down at elevated temperatures and was collected on the bottom of crucible. The chemical composition of copper ribbon after thermal treatment was analyzed by ICP-MS (Inductively coupled plasma mass spectrometry) and the purity of copper was found to be obtained up to about 96 wt.% regardless of temperatures. The cross-sectional area of the specimen was also examined by SEM (scanning electron microscopy) and EDX (energy dispersive X-ray microscopy).

Key words : Copper, Photovoltaic ribbon, Thermal treatment, ICP-MS

1. Introduction

Photovoltaic(PV) energy production is one of the most

promising and mature technologies for renewable energy production.¹⁾ It can be explained that photovoltaic(PV) modules are highly efficient and non-polluting power

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*Corresponding Author : Jei-Pil Wang (E-mail : jpwang@pknu.ac.kr)

Metallurgical Engineering, Pukyong National University, Yongdang Camp. Bld. #7 Room 311, 365 Namgu, Busan 608-739, Korea

Tel : +82-51-629-6341 / Fax : +82-51-629-6339

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generator associated with solar energy, and they do not produce any noise, not emit toxic gases, or not consume materials resources.²⁾ Therefore, many countries have already gained benefits through the PV industry due to long life time that usually lasts 20-25 years and the market of the PV modules is expanding rapidly. At the end of 2010 the cumulative photovoltaic capacity around the world reached more than 40 GW.³⁾ Although the market of the PV modules is expanding rapidly, unfortunately a spent PV module has affected serious environmental problems as well as illness in human since it contains hazardous materials such as Pb, Cd, Cr, and Bi. In present, most of spent PV modules have been discarded and buried under the ground without any recycling process, and the end-of-life PV modules should be therefore recycled under feasible technology and appropriate policy for environmental and economic benefits.⁴⁻⁷⁾

Many procedures for the recovery of valuable resources and for the removal of toxic materials from waste photovoltaic modules have been conducted using various methods.⁸⁻¹²⁾ S.M. Kang *et al.* studied a procedure for the recovery of silicon and tempered glass using organic solvent⁸⁾ and the feasibility of a sustainable photovoltaic thin film module recycling by means of (wet-)mechanical

processes was investigated by Berger W. *et al.*¹¹⁾ Furthermore, a study on the recovery of tellurium was conducted from CdTe-PV production and end-of-life scrap by Marwede M. *et al.*¹²⁾ Unfortunately, no researches have attempted to recovery of copper from the photovoltaic ribbon in solar module yet.

In the present study, copper was recovered from spent photovoltaic ribbon using thermal treatment process at the range of temperature of 300°C to 600°C under argon atmosphere. The thermal treatment method newly proposed was to melt down coating layer of PV ribbon that consists of tin and lead to separate it from the PV ribbon. The cross-sectional area and chemical composition of the specimen after thermal treatment was examined EDX (energy dispersive X-ray microscopy) and ICP-MS (Inductively coupled plasma mass spectrometry), respectively.

2. Experimental

Study on the recovery of copper from photovoltaic ribbon has been conducted at the range of temperature of 300 to 600°C under inert atmosphere using thermal treatment method. The photovoltaic ribbon mainly consists of high conductivity copper and solder coating layer of Pb-Sn alloy. The sample of copper ribbon was

Fig. 1. Chemical composition of photovoltaic ribbon analyzed by ICP and EDX.

Fig. 2. Experimental apparatus of thermal treatment setup.

obtained from KOSBON manufacturer and its width range of 1.00 mm to 4.00 mm and thickness range of 0.1 mm to 0.25 mm, respectively. The chemical composition of photovoltaic ribbon analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and electron dispersive x-ray spectroscopy (EDX) is shown in Fig. 1. It shows that the layer of Pb-Sn alloy was uniformly coated each side and its chemical composition was composed of 68.79 wt.% of tin and 31.21 wt.% of lead. The result of analysis of PV ribbon was shown to be 87.76 wt.% of copper, 5.25 wt.% of lead, and 6.15 wt.% of tin as well as small amounts of niobium and silver.

An experimental apparatus to separate coating layer of Pb-Sn alloy from photovoltaic ribbon using thermal treatment method is shown in Fig. 2. Ultra high purity argon gas was purged to maintain inert atmosphere inside reactor to prevent the photovoltaic ribbon from oxidation. A drierite(CaSO₄) was placed to remove humidity and magnesium chip was installed to minimize oxygen content of UHP argon gas. The partial pressure of oxygen in equilibrium at 500°C was shown as follows:

Thermodynamically, the coating layer in photovoltaic ribbon would be scarcely corroded and the layer will be melted down directly above melting temperature at

Fig. 3. Schematic diagram of the electric furnace and sample holder.

Fig. 4. Phase diagram of Pb-Sn alloy.

elevated temperatures.

A schematic diagram of electric furnace and a shape of specimen for removal of coating layer are illustrated in Fig. 3. The reactor (b) is made of SUS 301S which has oxidation and wear resistance at high temperatures and o-rings (c) were installed between body and cap to prevent leakage of gas. A cooling tube (d) was also placed right beside o-rings to cool it down. The specimens were placed inside alumina crucible and hanging from the rope and one side of the samples was contacted to the bottom of the crucible, which leads that coating layer melted will be accumulated to the bottom. The coating layer outside will be melted down at experimental conditions and copper inside will be maintained as it is. In the long run, it can be possible that the alloyed layer of Pb-Sn could be easily be separated from the photovoltaic ribbon and recovered as a form of powder and pure copper in photovoltaic ribbon was also obtained.

Fig. 5. (a) Melting down of coated layer and (b) EDX line scanning of the sample at 300°C.

Fig. 6. Chemical composition of photovoltaic ribbon obtained from spent solar cell. (A) Commercial photovoltaic ribbon (B) Spent photovoltaic ribbon.

3. Results and Discussion

The recovery of copper from the photovoltaic ribbon in solar cell has been conducted by thermal treatment at the range of temperature of 300 to 600°C under inert atmosphere. The range of temperature applied in thermal process was determined by chemical composition of coating layer and phase diagram of Pb-Sn alloy is shown in Fig. 4. According to the composition of 68.79 wt.% of Sn and 31.21 wt.% of Pb, the alloyed layer will be melted above 200°C and temperature range for this experiment was therefore established from 300°C to 600°C.

The thermal treatment to melt the coating layer down was conducted for 3 hours at elevated temperatures and cross-sectional area of the specimen after treated at 300°C was examined by EDX line scanning shown in Fig. 5. It is noted that the thickness of coating layer was found to be decreased from 20 μm to 5 μm owing to melting down of the layer during thermal treatment. The coating layer melted was found to be solidified at the bottom

Table 1. Chemical composition of the photovoltaic ribbon at each temperature

Temperature	Elements, wt. %				
	Cu	Pb	Sn	Nb	Ag
300°C	95.082	1.011	2.611	0.076	0.566
400°C	95.085	1.939	2.918	0.074	0.649
500°C	95.701	1.103	2.184	0.252	0.862
600°C	95.609	1.555	2.082	0.071	0.938

of the crucible and easily removed from the PV ribbon. The Pb-Sn alloy was found to be placed at the outside and copper was still dominant at the inside observed with based on the EDX line scanning.

The chemical composition of the photovoltaic ribbon after thermal treatment for 3 hours at each temperature under argon atmosphere was examined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the results are summarized in Table 1. It is noted that copper in PV ribbon was found to be a dominant

Table 2. Chemical composition of the photovoltaic ribbon obtained from spent solar cell after thermal treatment at each temperature

Temperature	Elements, wt.%				
	Cu	Pb	Sn	Nb	Ag
300°C	95.763	1.125	2.760	0.128	0.035
400°C	95.635	1.472	2.288	0.009	0.440
500°C	95.392	1.653	2.548	0.070	0.012
600°C	95.702	1.144	2.924	0.082	0.014

element composed of about 95 ~ 96 wt.% regardless of temperatures and minor elements such as tin, lead, silver, and niobium were detected in order. The content of copper in PV ribbon was increased from 87.75 wt.% to 95.70 wt.% at 500°C and the contents of lead and tin were decreased from 5.25 wt.% to 1.10 wt.% and from 6.15 wt.% to 2.18 wt.%, respectively.

The photovoltaic ribbons were obtained after dismantling process of spent solar modules and the chemical composition and cross-sectional area were examined by ICP-AES and EDX line scanning shown in Fig. 6. The content of copper taken out of spent photovoltaic modules was found to be about 87 wt.% that is similar value of copper content in commercial photovoltaic ribbon from KOSBON manufacturer. In addition, other elements such as lead, tin, niobium, and silver were also observed and their chemical contents were closely similar with commercial one. From the cross-sectional image the coating layer that consists of lead, tin, and silver was mainly observed one side since the other side might be stuck on the solar cell.

Table 2 summarizes the chemical composition of the photovoltaic ribbon obtained from spent solar modules after thermal treatment for 3 hours at each temperature under argon atmosphere was examined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). It is noted that copper in PV ribbon is dominant element accounting for about 95 ~ 96 wt.% at all range of temperatures and minor elements such as tin, lead, silver, and niobium were detected in order. The content of copper in photovoltaic ribbon was increased from 86.53 wt.% to 95.39 wt.% at 500°C and the contents

of lead and tin were decreased from 6.00 wt.% to 1.65 wt.% and from 6.94 wt.% to 2.55 wt.%, respectively. In the long run, the purity of copper in commercial ribbon and in spent ribbon was approached to about 96 wt.% and removal rates of lead and tin were found to be 79.04% and 64.6% in commercial ribbon and 72.15% and 63.26% in spent ribbon, respectively.

4. CONCLUSION

The recovery of copper from spent photovoltaic ribbon was carried out using thermal treatment method at the range of temperature of 300°C to 600°C under inert atmosphere. The coating layer consisted of lead of 68.99 wt.% and tin of 31.21 wt.% was melted down at elevated temperatures and copper was left in the photovoltaic ribbon. The chemical composition of copper ribbon after thermal treatment was analyzed by ICP-MS (Inductively coupled plasma mass spectrometry) and the purity of copper was found to be up to about 96 wt.% regardless of temperatures. In addition, removal rates of lead and tin were found to be 79.04% and 64.6% in commercial ribbon and 72.15% and 63.26% in spent ribbon, respectively.

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李 鎮 石

- 현재 한국에너지기술연구원 에너지 융합소재연구단 선임연구원

張 普 允

- 현재 한국에너지기술연구원 에너지 융합소재연구단 선임연구원

金 僑 秀

- 현재 한국에너지기술연구원 에너지 융합소재연구단 책임연구원

安 永 洙

- 현재 한국에너지기술연구원 에너지 융합소재연구단 책임연구원

姜 琦 煥

- 현재 한국에너지기술연구원 태양에너지연구단 책임연구원

王 帝 弼

- 동아대학교 금속공학과 학사
- University of Utah 금속공학 석사
- University of Utah 금속공학 박사
- LS-Nikko 동계연구소 기술연구소 선임연구원
- 현재 국립부경대학교 금속공학과 조교수