

融複合技術에 의한 廢콘덴서로부터 탄탈륨 再活用 基礎研究[†]

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A Preliminary Study on Tantalum Recycling from Obsolete Condenser by Multidisciplinary Process[†]

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요 약

폐콘덴서로부터 탄탈륨 음극을 회수하기 위하여 물리적 선별과, 염소가스와 사염화탄소를 이용한 기초 염화반응에 관한 연구를 수행하였다. Stamp mill을 이용한 파쇄, 요동테이블에서의 습식 비중선별 그리고 공기 분류를 통하여 탄탈륨 음극을 98% 회수할 수 있었다. 염소가스를 이용한 TGA분석에서 탄탈륨 음극의 최대 무게 감소는 60%였고, 사염화탄소에 의한 탄탈륨 음극의 염화반응은 탄탈륨 음극을 산화탄탈륨으로 변환한 후가 반응율이 높았다.

주제어 : 탄탈륨, 재활용, 폐콘덴서, 물리적 선별, 염화반응.

Abstract

For recycling of tantalum from obsolete condenser, physical separations and chlorination of tantalum scraps with Cl₂ and CCl₄ were investigated. The recovery ratio of tantalum from obsolete condenser was 98% by using a multidisciplinary process of crushing by stamp mill, wet gravity separation by the shaking table, and air classification. In the chlorination reaction of non-oxidized Ta anode with Cl₂, the highest weight loss ratio is at least 60%, while in the chlorination reaction of Ta anode with CCl₄, the reaction rate for the oxidized Ta anode is faster than that of the non-oxidized Ta anode.

Key words : tantalum, recycling, condenser, physical separation, chlorination.

1. Introduction

Tantalum is one of the rare elements in the earth's crust. This rarity and the depletion of high-grade ores put emphasis on recycling of tantalum. Tantalum powder has been mostly consumed in capacitors. It therefore is very important to recover tantalum from obsolete condenser.

The early tantalum condenser was mainly in dip type, but in the recent it has been changed largely into chip type and small size. The chip type condenser is

composed of two parts, electrode and shielding resin. The electrode contains Ta anode and lead frame composed of nickel alloy. To effectively recover tantalum from the obsolete electrode, it is required to separate Ta anode from shielding resin¹⁾. Crushing by roll crusher, magnetic separation and air classification provide the effective separation between Ta anode and resin²⁾.

Ta anode contains not only Ta but MnO₂-dielectric substance, Ag, and graphite-cathode. It accordingly is difficult directly to prepare high-grade tantalum without chemical process. In this study, the chlorination reaction of Ta anode was adapted as a chemical process. The chloride process for dressing and processing rare metal

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concentrates occupies an important position in the metallurgical technology. The chloride process has been used in the treatment of tantalum bearing ores^{3,4}. Tantalum contained in Ta anode is covered with thick tantalum oxide layer. Metallic tantalum and chlorine

gas react well even at low temperature of 400°C, but the direct reaction between tantalum oxide and chlorine without a reducing agent such as carbon is not feasible thermodynamically under 1000°C. On the other hand, it was recently reported that chlorination

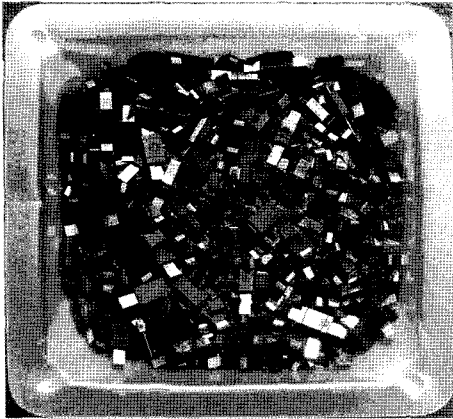


Photo 1. Chip type condenser.

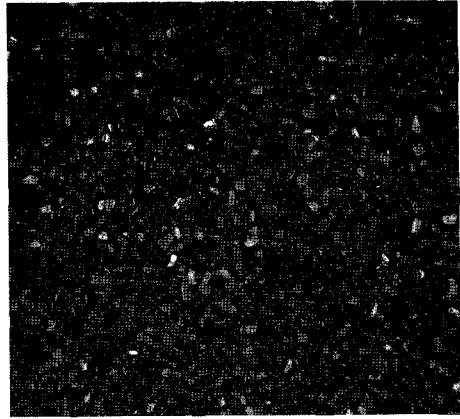


Photo 2. Recovered Ta anode.

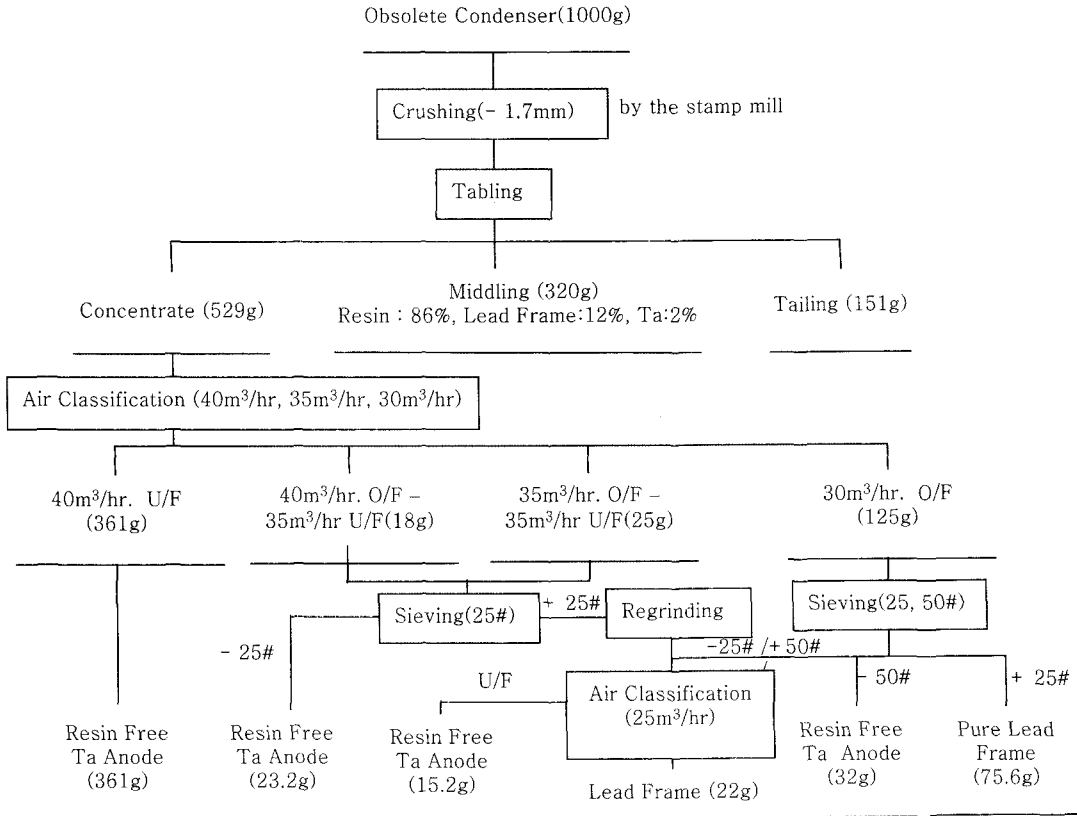


Fig. 1. Schematic diagram of the process for separation of Ta anode from obsolete condenser.

between tantalum oxide and carbon tetrachloride could be carried out at low temperature below 500°C as the following reaction equation^{5,6}.



Therefore, in this study, the chlorination of Ta anode using a micro thermogravimetric analysis (TGA) unit was investigated. Here, chlorine and carbon tetrachloride gas are used as a reactant gas, respectively.

2. Experimental

2.1. Physical separation of Ta anode

The sample used in this study is the scrap of chip type condenser shown in Photo 1.

Fig. 1 schematically shows a process flow sheet carried out for separating Ta anode from obsolete condenser. The obsolete condenser was firstly crushed down under 1.7 mm(12#) to bare Ta anode by stamp mill and followed by wet gravity separation using shaking table(Wilfley No 13B) to separate metal part. After that, the metal part was again separated to Ta anode and lead frame by the air classifier of zig-zag type(1-40 MZM, Alpine, Germany). The Ta anode recovered from physical separation process is shown in Photo 2.

2.2. Chlorination

Experiments were carried out in a TGA unit to measure the rate of chlorination reaction of Ta anode with reactant gases such as chlorine and carbon tetrachloride.

As shown in Fig. 2, the apparatus consisted of a reactor and a gas delivery system together with an electro-balance that continuously recorded the weight changes taking place during the reaction. The reactor was a silica tube of 1.5cm inner diameter and 25cm length. In the course of the experiments, nitrogen gas was purged continuously through the balance chamber to prevent the intrusion of reactant gas and heat into it. Especially, in order to blow carbon tetrachloride gas into the reactor, liquid carbon tetrachloride was firstly pumped into a flask, and then vaporized at 423°K ($\pm 1^\circ\text{K}$). The reactant gas was mixed with nitrogen and passed into the reactor, and the partial pressure of reactant in the gas mixture was determined by adjusting the amount of reactant blown into the flask. The gas temperature in the reactor was measured by Pt-13%Rh/Pt thermocouple. A uniform temperature profile of $\pm 1^\circ\text{K}$ was achieved over 2cm length of the reaction tube.

Two types of sample were used in chlorination. The one is the raw Ta anode obtained from physical

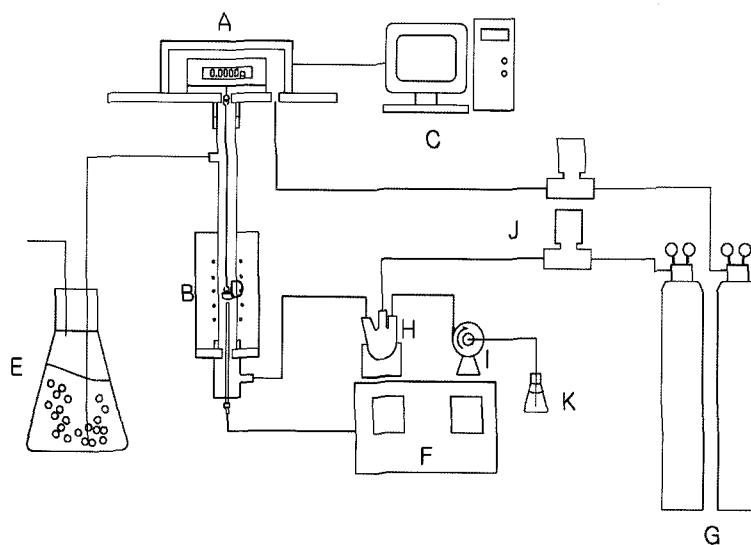


Fig. 2. Schematic diagram of the experimental apparatus. A: Micro balance, B: Furnace, C: Data collector D: Sample tray, E: NaOH solution, F: Temperature controller, G: $\text{N}_2(\text{g})$ cylinder, H: Carbon tetrachloride evaporator, I: Volumetric pump, J: Mass flow controller, K: Carbon tetrachloride.

separation, called non-oxidized Ta anode. The other is the Ta anode oxidized at 850°C in air, called oxidized Ta anode.

Powder samples weighing 35~45 mg placed on a shallow holder were used in the TGA experiments. The sample holder was a silica basket. By conducting preliminary experiments, it was also found that the reactor tube and sample holder did not react with chlorine and carbon tetrachloride gases in the temperature ranges between 723 and 1173°K.

3. Results and Discussion

In the physical separation process shown in Fig. 1, the recovery ratio of Ta anode contained in the obsolete condenser was calculated as 98% from material balance. The chemical composition of the concentrated Ta anode is shown in Table 1.

The Ta anodes were oxidized at 850°C for 3 hr and 6hr under atmosphere. The Ta anodes changed from black granule to white fine powder with oxidizing reaction. Fig. 3 represents XRD peaks of the oxidized and the non-oxidized Ta anode samples. In the study, these samples are used for investigating the chlori-

Table 1. Chemical composition of the recovered Ta anode.

Component	Ta	Mn	Ni	Ag
wt%	72.2	7.7	1.4	0.13

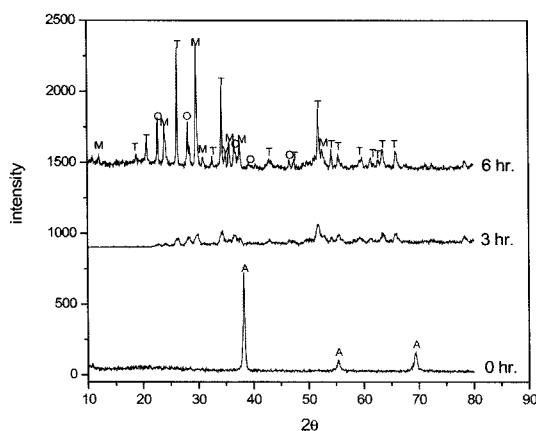
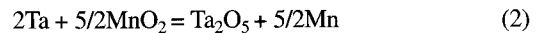


Fig. 3. XRD peaks of Ta anode with time of oxidation at 850°C under atmosphere. A: metallic Ta, M: manganese tantalate, O: tantalum pentoxide, T: manganese tapiolite.

nation reaction of the concentrated.

In the crushing obsolete condenser, fair portions of Ta anode chips were burned by shock of stamp mill. Due to that tantalum is more active metal than manganese(MnO₂) contained in Ta anode as dielectric substance, metallic tantalum contained in the anode chips was converted to tantalum oxide as the following reaction equation:



The production of Ta₂O₅ may affect a bad effect for the chlorination reaction of Ta anode with chlorine gas because Reaction (3) is not feasible thermodynamically at the low temperature below 1000°C.

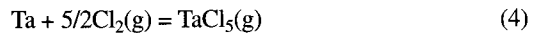


Fig. 4 shows TGA curves of the chlorination reaction between the non-oxidized Ta anode and Cl₂(P_{Cl₂}=0.5) at various temperatures. As shown in Fig. 4, the highest weight loss is at least 60%. This is the reason that the metallic tantalum reacts with chlorine gas such as Reaction(4). Here, the solid residue might be 24% of MnCl₂ that has high boiling point and 15% of Ta₂O₅ of the reactivity which is very low with chlorine gas, which is calculated by using the chemical composition of Mn and Ta in Table 1. Also, in the experiments, the reaction rate between Cl₂ and Ta anodes at the low temperature range below 800°C had poor reproducibility.

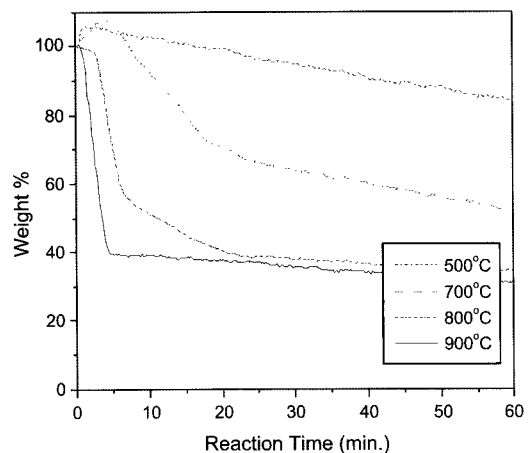


Fig. 4. TGA curves of chlorination between non-oxidized Ta anode and Cl₂(P_{Cl₂}=0.5) at various temperatures.

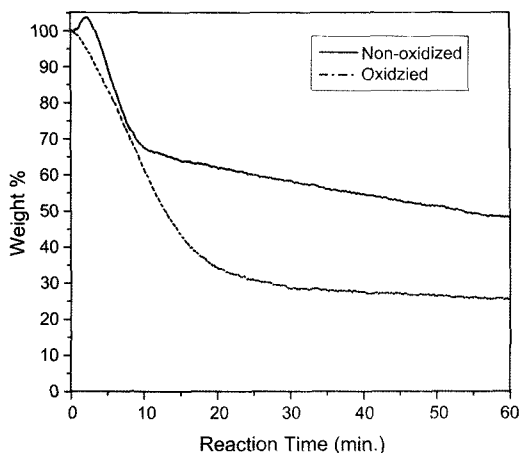


Fig. 5. TGA curves of chlorination between CCl_4 and oxidized or non-oxidized Ta anode at Temp.=500°C and P_{CCl_4} =0.5.

It was considered by the fact that the reaction rate at the low temperature range below 800°C depends upon the geometry of Ta anode that is covered with thick oxide layer. At the high temperature range, 900-1000°C, the reproducibility of the reaction rate data is good. That is the reason why the reaction rate is very fast to be able to neglect the geometry effect as shown in Fig. 4.

On the other hand, Fig. 5 shows TGA curves of the chlorination reaction between CCl_4 and Ta anodes at 500°C. Shown as Fig. 5, the reaction rate for the oxidized Ta anode is faster than that of the non-oxidized Ta anode. It would be explained by the fact that when the metallic Ta reacts with CCl_4 , the carbon produced by the reaction would be covered the surface of the metallic Ta particles.

4. Conclusion

In order to separate Ta anode from obsolete condenser, the multidisciplinary process of crushing by stamp mill, wet gravity separation by the shaking table, and air classification is very effective and provides the high recovery yield over 98%. Also, by crushing the obsolete condenser, the metallic tantalum contained in the obsolete Ta anode was partially converted to tantalum oxide. In the chlorination reaction of non-oxidized Ta anode with Cl_2 , the highest weight loss ratio is at least 60%. In the chlorination reaction of Ta anodes with CCl_4 , the reaction rate for the oxidized Ta anode is faster than that of the non-oxidized Ta anode.

Reference

1. Nobuaki Sato *et al.*, 1990: Pyrometallurgical Treatment of Tantalum Capacitor Scrap via Chlorides, *Bulletin of the Research Institute of Mineral Dressing and Metallurgy Tohoku University*, **47**(2), pp. 96-104.
2. Kim, S. *et al.*, 2003: Recovery of Tantalum Anode from Waste Tantalum Condenser by Air Classification, *J. of Korean Inst. of Resources Recycling*, **12**(3), pp. 3-12.
3. Zhulanov, O. N. *et al.*: 1997, New Aspects in Development of the Chloride Process for Tantalum-Niobium Raw Materials, *Russian Journal of Non Ferrous Metals*, **38**(10), pp. 33-37.
4. Gonjalez, J. *et al.*, 1998: Chlorination of Niobium and Tantalum Ore. *Thermochimica Acta*, **311**, pp. 61-69.
5. Jena, P. K. *et al.*, 2001: Study on the Kinetics of Carbon Tetrachloride Chlorination of Tantalum Pentoxide, *Metall. Mater. Trans. B* **32B**, pp. 801-810.
6. Kim, S. *et al.*, 2005: Study on the Kinetics of the Chlorination Reaction of Tantalum Pentoxide by Carbon Tetrachloride, *J. of Kor. Inst. Met. & Mater.*, **43**(5), pp. 389-392.

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