Influence and Effect of Pyrolysis with Additives in Tantalum Capacitors

Rinon Shimizu, Ryuki Hanazawa, and Naoyuki Morita

Abstract—In recent years, the demand for tantalum capacitors has been increasing due to the miniaturization of electronic devices. Tantalum capacitors, which use the rare metal tantalum as the capacitor element, are used in electronic devices such as cell phones because they are smaller and have a higher capacity than conventional capacitors. In Japan, there are reports that minerals containing rare elements are being extracted from discarded electronic and electrical equipment to produce medals for the 2020 Tokyo Olympics. In Japan, many used electrical products containing rare elements are discarded, and these metals are called urban mines. The tantalum contained in tantalum capacitors accounts for 40% of the total mass of the sintered material and is expected to be recycled from discarded products. However, tantalum capacitors are covered with a hard mold resin of acrylonitrile-butadiene-styrene (ABS) resin, which is chemically and physically stable. However, due to its nature, ABS resin is difficult to destroy and has not been recycled. In this study, hydrotalcite (HT) \((\text{Mg}_{6}\text{Al}_{2}(\text{OH})_{16}\text{CO}_3 \cdot \text{MH}_2\text{O})\) was used to extract tantalum from the sintered tantalum capacitor by pyrolysis. HT was added to the tantalum capacitor and placed in a metal reactor and subjected to pyrolysis at 550°C in nitrogen to determine if the sintered tantalum was susceptible to fracture. It is presumed that the bromine gas generated from the ABS resin of the tantalum capacitor was trapped by the HT and the mold resin of the capacitor became residual carbon.

Index Terms—Tantalum capacitors, hydrotalcite, pyrolysis.

I. INTRODUCTION

In recent years, tantalum has become an important mineral resource for the electronics industry. However, the tantalum mineral industry has traditionally been considered "shrouded in secrecy". Tantalum capacitors are an essential mineral resource for high-performance electronic devices, such as smartphones, and the demand for tantalum capacitors has grown annually as electronic devices become smaller. Tantalum is a rare metal that is difficult to extract for technical and economic reasons. The securing of a stable supply is considered an important policy issue [1]. Tantalum production from coltan, which is a mineral that is rich in tantalum, is considered the primary production route. However, because of the uneven distribution of rare metals, technical and economic reasons. The securing of a stable supply has undergone a major change since the 1970s. As a result, the demand for rare metals, which are essential resources in a variety of electronic devices, has increased. However, because of the uneven distribution of rare metals, prices and production are not stable [2]. Tantalum capacitors, which are composed of high-concentration sintered tantalum, are smaller and more efficient than other types of capacitors and are used in many products, such as personal computers, servers, and small home appliances. In recent years, the Japanese government has designated 14 priority minerals for recycling, including tantalum as one of the five most important minerals for intensive recycling [3]. Large amounts of used electrical appliances that contain rare metals are being disposed of. In Japan, disposal sites are termed "urban mines" because rare metals are buried in cities. Reports that the Tokyo 2020 medals were made from metals from urban mines were of great interest. Based on this background, it is desirable to develop a new technology to separate and recover resources, such as rare metals in electrical appliances and electronic components [4]. A tantalum capacitor consists of three main components: sintered tantalum powder that is used as an electrode, mold resin that is used as a cover for the sintered body, and terminals that are connected to the electrodes. The recovery of tantalum from tantalum capacitors is achieved by recovering the tantalum sintered body that is encompassed by the capacitor. However, the challenge is to destroy the mold resin, which is chemically and physically stable. Combustion [5] and solubilization [6] have been proposed as methods for the treatment of mold resin, but several challenges have been identified with these methods, including high combustion temperatures, high pressure using pressure reactors, and the formation of harmful halogenated compounds. Therefore, alternative treatment methods are desired [7]. In this study, synthetic hydrotalcite (HT), which is expected to function as an alkali catalyst, was added to a tantalum capacitor and pyrolyzed at 550°C to recover sintered tantalum. An abundance of literature exists on the basic investigation of pyrolysis and the chemical recycling of waste plastics [8]-[16]. However, the acrylonitrile-butadiene-styrene (ABS) mold resin that is used in tantalum capacitors has physical and chemical stability issues and contains halogenated flame retardants that produce toxic gases when heat treated [17]. The pyrolysis of halogenated plastics has been carried out by using a carbon composite of calcium carbonate (calcium-C) [18]. The quality of commercial hydrogenation catalysts DHC-8 and pyrolysis oil that contain these catalysts was examined and improved and showed that most toxic halogenated compounds were decomposed, and the halogens were released as gases. In the recycle of tantalum capacitors, argon pyrolysis enabled the separation of the mold resin into...
product oil and gas [19] [20]. It has been reported that 94.32 wt% of the mold resin was removed by vacuum pyrolysis [21]. Sintered tantalum recovery from spent tantalum capacitors using steam gasification with sodium hydroxide has also been performed [22]. However, no reports mention that halogenated gases have been produced, although resin destruction has been reported. Plastics with flame retardants that contain halogenated compounds require special treatment. Flame retardants that can reduce the flammability of plastics contain polybrominated compounds that are harmful to humans. Examples include polybrominated dibenzoparadioxins and polybrominated dibenzofurans [23]. Many plastics that are used in mold resins are composed of ABS, and typically contain antimony trioxide as a synergist for the flame-retardant bromine compound because its addition allows the amount of flame retardant to be reduced significantly from the amount that would otherwise be required for ignition. Special treatment is required because of the health hazards of these additives. Extensive literature is available on the pyrolysis of ABS [24]-[26]. When tubular reactors are used for the pyrolysis of ABS that contains brominated flame retardants, bromine remains in the intermediate distillates and heavy oil components [25]. It has also been reported in a study on the thermal degradation of ABS that the use of a half-batch reactor results in the enrichment of the contained brominated flame retardants into residual carbon [24]. We reported that HT addition in the pyrolysis of brominated plastics reduced the content of bromine compounds in the product oil [27]-[29]. The effect of HT addition with different elemental composition ratios in the pyrolysis of brominated polystyrene was also reported [30]. HT is classified as a layered double hydroxide that is composed of metal complex hydroxides and consists of divalent Mg$^{2+}$ and trivalent Al$^{3+}$ host layers and anionic species in the interlayer guest layers (Fig. 1). HTs have received increasing attention in recent years as materials for catalysis and gas removal, and as ion exchangers. The high anion exchange capacity of HT, which is comparable with that of organic ion exchange resins, has attracted much attention and it has been used as an adsorbent to remove various contaminants from aqueous solutions. The adsorption of inorganic anions such as borate, nitrate, fluoride, phosphate, sulfate, chromate, arsenate, and selenate on HT has been investigated. HT has also attracted attention as a catalyst and has been reported to increase the yield from 62% to 77% in biodiesel fuel production. Recently, it has been reported that the catalytic properties of HT can be improved by setting the molar ratio of divalent Mg$^{2+}$ and trivalent Al$^{3+}$ as a parameter [31]-[34]. In this study, HT with Mg/Al$_2$ = 4.5 was used in the pyrolysis of tantalum capacitors to study its effect and effectiveness.

### II. EXPERIMENTAL

#### A. Materials

The tantalum capacitor (6.0 mm × 3.2 mm × 2.5 mm, model number: ESVC1V475M) was from a trading company and was not from a conflict zone (Fig. 2). A typical tantalum capacitor consists of sintered tantalum (40%), mold resin (44%), and others (16%) (Fig. 3). The composition of the mold resin consists of fused silica (70%) OCN (o-Cresol novolac)-type epoxy resin (15%), phenolic novolac resin (7%), and flame retardant (10%) (Fig. 4) [14].

The additive, synthetic HT (KW-1000) was from Kyowa Chemical Industry Co. The composition ratio is shown in Table I.

| TABLE I: COMPOSITION RATIO OF HT |
|----------------------------------|
| Al$_2$O$_3$ (wt%) | MgO (wt%) | Mg/Al$_2$O$_3$ | Na (wt%) |
|-----------------|-----------|---------------|----------|
| 19.3            | 35.1      | 4.60          | 0.02     |

Mg/Al$_2$=4.5

#### A. Pyrolysis Experiments and Procedures

The sample consisted of 2 g of tantalum capacitor (TC) with synthetic HT (KW-1000; Kyowa Chemical Industry Co., Ltd.) as an additive. A mixture of 2 g of the sample with various amounts of HT was used. For comparison, 2 g of sodium hydroxide (Wako Co., Ltd.) and 2 g of sea sand (methanol-washed, 425–850 μm, Wako Co., Ltd.) were added. The experimental conditions are shown in Table II.
The experimental setup that was used in this study is shown in Fig. 5. The mixed sample was placed in the metal reactor and nitrogen gas was flowed at 50 mL/min to remove oxygen from the reactor, followed by nitrogen replacement for 60 min. After nitrogen replacement, the nitrogen gas was stopped, and the pyrolysis experiment was carried out. The sample part of the metal reactor was measured as the decomposition temperature using a thermocouple, and the temperature was raised to 550°C at 5°C/min. After reaching 550°C, the sample was allowed to cool naturally immediately. The gas that was generated during pyrolysis passed through the cooling tube and was condensed and collected as product oil in a collection vessel. The non-condensable gas was collected in a gas pack by bubbling alkaline aqueous solution and measuring the decomposition product gas.

B. Recovery of Sintered Material after Pyrolysis

The residue after pyrolysis was mixed with distilled water in the ratio of 3 to 100 and stirred for 120 min at 200 times per minute to recover the calcined tantalum (Fig. 6).

C. Analysis

The product oil could not be obtained by pyrolysis. The HT residue was analyzed by energy dispersive X-ray spectroscopy (EDS, S2RANGER, BRUKER) for surface observation and bromine determination. The HT after pyrolysis was analyzed by an X-ray structure analyzer (XRD, MiniFlex, RIGAKU) for structural analysis. The alkaline solution after the experiment was subjected to qualitative and quantitative analysis of bromine by using an ion chromatography system (PIA-1000, SHIMADZU). The gas produced, which was less than 1 L, was analyzed qualitatively and quantitatively by a gas chromatography system (GC-2014 SHIMADZU).

III. RESULTS AND DISCUSSION

A. Tantalum Capacitor after Pyrolysis

The state of the tantalum capacitor after pyrolysis is shown in Table III. The left side shows the state after pyrolysis and the right shows the state after stirring.

B. Recovery of Sintered Material after Pyrolysis

Although cracks and other changes were observed by pyrolysis treatment of the tantalum capacitor, only condition III, in which HT was added in a ratio of 2:1 to the tantalum capacitor, could destroy the mold resin. By stirring, sintered tantalum could be recovered in conditions II and III.
B. Residue

The bromine content of HT in the residue was determined by observing the HT surface with an energy dispersive X-ray analyzer (EDS, S2RANGER, BRUKER) to monitor Br in the residue (Fig. 7). To verify the extent to which pyrolysis affected the HT structure, HT before pyrolysis and the residue of condition III were analyzed by using an X-ray structure analyzer (XRD, MiniFlex, Rigaku) (Fig. 8).

C. Gas Production

The volume of gas that was generated by pyrolysis was less than 1 L for all conditions. The collected gas was analyzed qualitatively and quantitatively by gas chromatography (GC-2014 SHIMADZU). Qualitative and quantitative analysis of the NaOH solution after pyrolysis was performed by ion chromatography (PIA-1000, SHIMADZU), and Br was not detected when HT was added (Table IV).

| TABLE IV: Qualitative Analysis of NaOH Aq. Solution by IC |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|            | I           | II          | III         | IV          | V           | VI          | VII         |
| Br         | +           | nd          | nd          | nd          | +           | +           | +           |
| nd: not detected |

IV. Conclusions

Synthetic HT (KW-1000, Mg/Al₂ = 4.5) was added to the tantalum capacitor. The mold resin was destroyed by pyrolysis at 550°C, and the encapsulated sintered tantalum was recovered easily. It is suggested that the rate of addition affects the recovery.

It is speculated that the catalytic effect that was retained by the HT is why the mold resin was destroyed by synthetic HT addition. The synthetic HT is a composite hydroxide of magnesium and aluminum; therefore, it is thought to have a catalytic effect. In addition, HT holds water between layers. ABS resin, which is a mold resin, is prone to hydrolysis under conditions where water is present. Therefore, it can be inferred that the decomposition was accelerated in the metal reactor of this study because of the decomposition reaction that was caused by heat and the hydrolysis reaction that was caused by the interlayer HT water.

The tantalum capacitors after pyrolysis was destroyed by sputtering. In conditions III and IV, the mold resin was destroyed before the sputtering operation, and in the pyrolysis with HT, the optimum addition rate was 0.25–0.5 to the mass ratio of the tantalum capacitors. It is suggested that the optimum addition amount existed at an addition rate of 0.25–0.5 to the mass ratio of the tantalum capacitors.

The halogen gas from thermal decomposition is expected to have been captured by the HT not because of its anion exchange capacity of the HT, but because of the acid–base reaction (neutralization reaction) between the basic HT and the acidic bromine gas. If HT captures anions by its anion adsorption capacity, it is unlikely that captured bromine is observed on the surface because it is retained between the HT layers. Because bromine was observed on the HT surface after pyrolysis in this study, it is inferred that the neutralization reaction by the acid–base reaction occurred and bromine was recovered, as described above.

The XRD analysis of the HT indicates that the layered structure, which is the characteristic structure of HT, collapses after pyrolysis at 550°C. XRD analysis of the HT suggests that the layered structure, which is characteristic of HT, breaks down after pyrolysis at 550°C. However, the function of breaking the mold resin of the tantalum capacitor and capturing the bromine gas produced remains intact.

These results suggest that HT addition to the tantalum capacitor at a ratio of 0.25–0.5 to the tantalum capacitor mass and pyrolysis can easily destroy the mold resin of the tantalum capacitor and collect the bromine gas that is produced as a residue.

CONFLICT OF INTEREST

All authors declare that: (i) no support, financial or
otherwise, has been received from any organization that may have an interest in the submitted work; and (ii) there are no other relationships or activities that could appear to have influenced the submitted work.

AUTHOR CONTRIBUTIONS

R. Shimizu and R. Hanazawa performed the experimental work and data analysis. The wording of the final paper was agreed upon by all authors.

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