Tantalum recycling from waste of electrical and electronic equipment

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Abstract. The possibility of tantalum recycling from waste of electrical and electronic equipment was investigated. Study was carried out using basic physical and chemical methods, ie. mechanical separation via crushing, leaching of silver layer in diluted HNO_3, grinding and oxidation of anodes and thermic reduction with metallic reducing agent. A recovery rate of anodes was determined at 96%, and recycling efficiency of tantalum to pure form was determined more than 50%. Also was made mass balance.

1 Introduction

The necessity of miniaturization of electrical and electronic equipment led to the search for the capacitors on the performance of providing relatively high electrical capacity and stability under working conditions. Metallic tantalum is used for the manufacture of capacitors, because from this metal can be produced a dielectric layer with a high electric capacity.

Typical tantalum capacitor (Figure 1), otherwise Ta and Ta_2O_5, also consists of other factors, such as: MnO_2 (solid electrolyte), Ag (high chemical resistance layer), graphite (layer between MnO_2 and Ag), Sn and Ni (components of solder and wires), epoxy resin (protective layer against mechanical damage). Not only the form of tantalum (pure metal and oxide), but also other above-mentioned components, determines the process of recycling of tantalum capacitors.
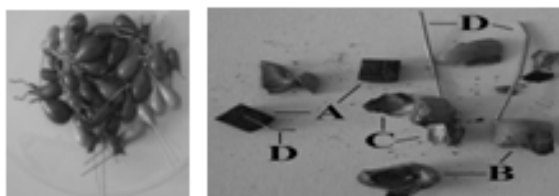

Figure 1. Tantalum capacitors (left), broken capacitor (right): tantalum anode (A), epoxy resin (B), silver foil (C), wires (D)

There are many methods of tantalum recycling from waste electrical and electronic equipment (WEEE). Acknowledged practice is mechanical separation of tantalum by breaking and milling [1, 2]. Otherwise, it is possible to burn the epoxy resin in $500 \div 1000^0C$ for $1 \div 5$ hours oxidation is also obtained Ta_2O_5 [2-4], which can be reduced most commonly with Na, Mg or Ca [4, 5]. Tantalum capacitors can be leached e.g. in aqua regia, concentrated HCl, NaOH or KOH [1]. The leaching capacitors by using iron chlorides ($FeCl_x$) tantalum chloride is obtained, which is then reduced with

Mg [2]. Other methods, such: exfoliation of printed circuit boards containing capacitors [6], tantalum recovery by Cu-Fe-C alloy doped Fe_2O_3 [3], the electrochemical reduction of dissolved tantalum in molten salt by dysprosium ions [5], are reported.

Typically, the tantalum recycling from WEEE (mainly form printed circuit boards) is a multistep process, and the final product may be impure with other elements; therefore, it has still not been development a simple and effective recycling process.

The aim of this study was to develop a process of tantalum recycling from WEEE. Special attention was paid to the use of diluted solutions, low temperature and safe reagents.

2 Experimental

Development process of tantalum recycling from WEEE consists the following steps:

1. coarse breaking the capacitors and grinding the tantalum anodes,
2. leaching anodes in diluted HNO_3,
3. grinding the anodes,
4. oxidation,
5. pressing the oxidised anodes with reducing agents,
6. thermic reduction.

The material used for this study was tantalum capacitors to though-hole mounting (Figure 1), weighting approx. 210 g.

Leaching solution was 8M HNO_3 (700 ml). Reducing agents were: Al, Mg and Si (all technical grade; 1.344, 1.049, 1.815 g, respectively).

2.1 Coarse breaking and grinding

Capacitors were broken (Figure 1), anodes were mechanically separated from wires and resin and grinded. Due to the generation of harmful combustion products of epoxy resin [2-4] was not used from burning process.

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2.2 Leaching

Leaching was primarily aimed at get rid of Ag from the anodes:

$$4Ag_{foil} + 6HNO_3 \rightarrow 4AgNO_{3dissolved} + \uparrow NO + \uparrow NO_2 + 3H_2O \quad (1)$$
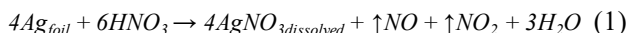
Efficient leaching of Ag requires concentration of HNO_3 above 3M: the best in the range 8÷10M. In addition, the epoxy resin pieces float on the solution surface - they were mechanically removed.
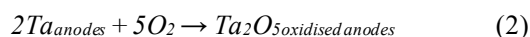
Leaching was lasted 12 h.

2.3 Grinding the anodes

Deprived of Ag and most of resin, anodes were grinding. The purpose of grinding was to allow uniform for future oxidation.

2.4 Oxidation

After oxidation was obtained anodes to Ta_2O_5 "concentrate" [1-3]:

$$2Ta_{anodes} + 5O_2 \rightarrow Ta_2O_{5 oxidised anodes} \quad (2)$$

In addition, the residual epoxy resin reacts with oxygen to form Si and additionally are formed combustion products (CO_2 and H_2O) [1], and graphite layer - to CO_2.

Oxidation was carried in furnace at 900^0C for 1h.

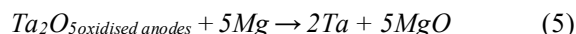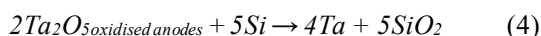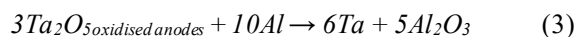## 2.5 Pressing the oxidised anodes with reducing agents

Reduction conditions must be such that the material containing Ta_2O_5 (oxidised anodes) had a minimal physical contact with bottom and wall of crucible and other impurity sources [4]. For this purpose, the oxidised anodes (per 12 g) together with respectively reducing agents were pressed to moulded pieces.

It has been applied 20% excess of reducing agents relative to the mass resulting from the stoichiometry.

Pressing made in conditions 160÷240 MPa.

2.6 Thermic reduction

Reducing agents were Al, Mg and Si (all reduce of Ta_2O_5 in process conditions, have high affinity to oxygen and are safe to use). Reductions are as follows:

$$3Ta_2O_{5 oxidised anodes} + 10Al \rightarrow 6Ta + 5Al_2O_3 \quad (3)$$

$$2Ta_2O_{5 oxidised anodes} + 5Si \rightarrow 4Ta + 5SiO_2 \quad (4)$$

$$Ta_2O_{5 oxidised anodes} + 5Mg \rightarrow 2Ta + 5MgO \quad (5)$$

The reduction with Al and Mg were carried at 650^0C, and with Si at 1000^0C for 9 h duration under Ar atmosphere.

3 Results

3.1 Mass balance

Table 1 shows the mass balance of materials starting from breaking the anodes to thermic reduction.

Tantalum anodes losses were resulted of the layered construction and structure of capacitors. Pressing the oxidised anodes with reducing agents is associated with material loss of 8%.

Table 1. Mass balance in steps: coarse breaking and grinding (1), leaching (2), grinding (3), oxidation (4), pressing (5) and thermic reduction (6) (masses in g)

steps	materials/wastes				
	main stream			wastes / losses / others	
	capacitors 209.554			waste 99.530	
1	anodes 109.485			waste 0.420	
2	leached anodes 106.045				
3	grinded anodes 104.745			anodes not oxidised 8.913	losses 1.300
4	anodes to oxidation 95.832				
	oxidised anodes 106.668			in next step was used 36.000 of oxidised anodes	losses 0.082
5	mixture oxidised anodes &:				
	Al 13.344	Si 13.049	Mg 13.815		
	moulded piece with:			losses 0.089, 0.294, 1.044 (moulded pieces with Al, Si and Mg respectively)	
	Al 13.245	Si 12.755	Mg 12.771		
6	moulded pieces after reduction with:			losses 0.314, 0.247, 0.397 (moulded pieces with Al, Si and Mg respectively)	
	Al 12.931	Si 12.508	Mg 12.374		

3.2. Recovery rate of anodes

Based on data from Table 1, was estimated recovery rate of anodes:

$$\eta_1 = m_{grinded\ anodes} / m_{anodes} \cdot 100\% = 104.745 / 109.485 \cdot 100\% = 95,7\% \approx 96\% \quad (6)$$

where: $m_{grinded\ anodes}$ - mass of grinded anodes, and m_{anodes} - mass of obtained (recovered) anodes (all masses in g).

3.3 Analysis of the chemical composition

The capacitors consists mainly of Ta and Mn, less Ag and Sn (Figure 2A). The confirmation of leaching Ag, Sn and also Mn in HNO_3 is showed in Figure 2. These impurities are passed to solution through chemical and mechanical ways. In oxidised anodes are: Ta_2O_5, manganese tantalum oxide and $Mn(Ta_2O_6)$ (Figure 3), which are oxidation products. Oxidation is resulted in increased concentration of Ta (Figure 2 and Table 2). After thermic reduction, only in case of moulded piece with Mg was obtained pure Ta (Figure 4). The reduction was incomplete, because beside Ta is also formed a complex compound $(Mn_{0.6}Mg_{1.4})Mg_2(Ta_2O_9)$. Mg was also in MnO form (Figure 4). The main impurities are Mn and Mg (Table 3).

Table 2. Comparison of metallic elements contents (% mas.): leached, oxidised and reduced anodes - XRF MINIPAL analysis (without pattern analysis)

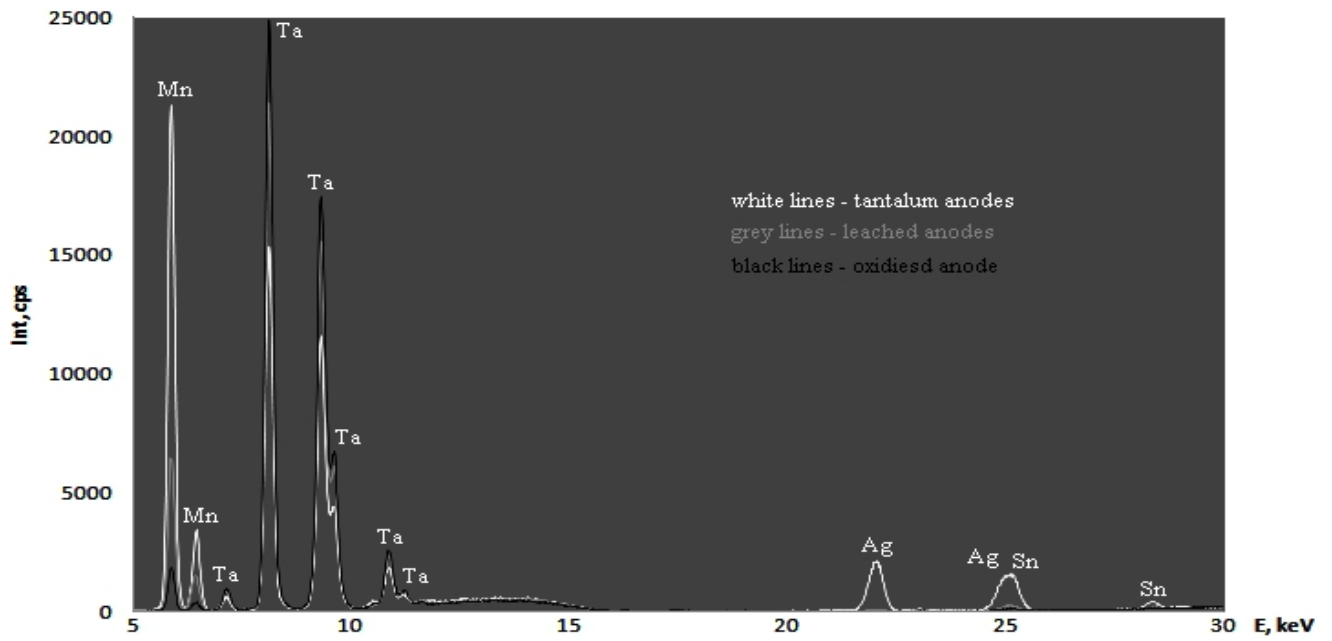|	Mn	Ag	Sn	Ta	Mg
leached anodes	16.5	0.4	1.3	81.8	-
oxidised anodes	4.8	0.2	0.2	94.8	-
reduced moulded piece with Mg	4.2	0.2	0.2	85.6	9.7

Figure 2. X-ray fluorescence spectroscopy analysis: tantalum anodes (white), leached anodes (grey), oxidised anodes (black)
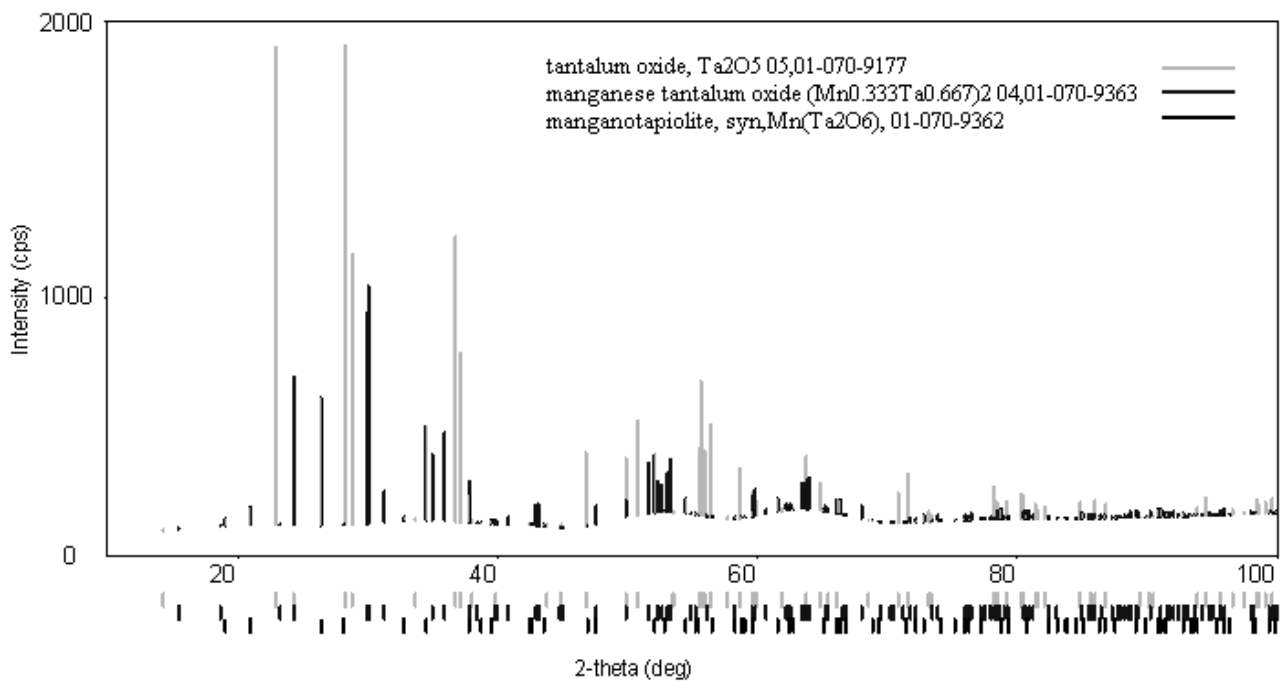

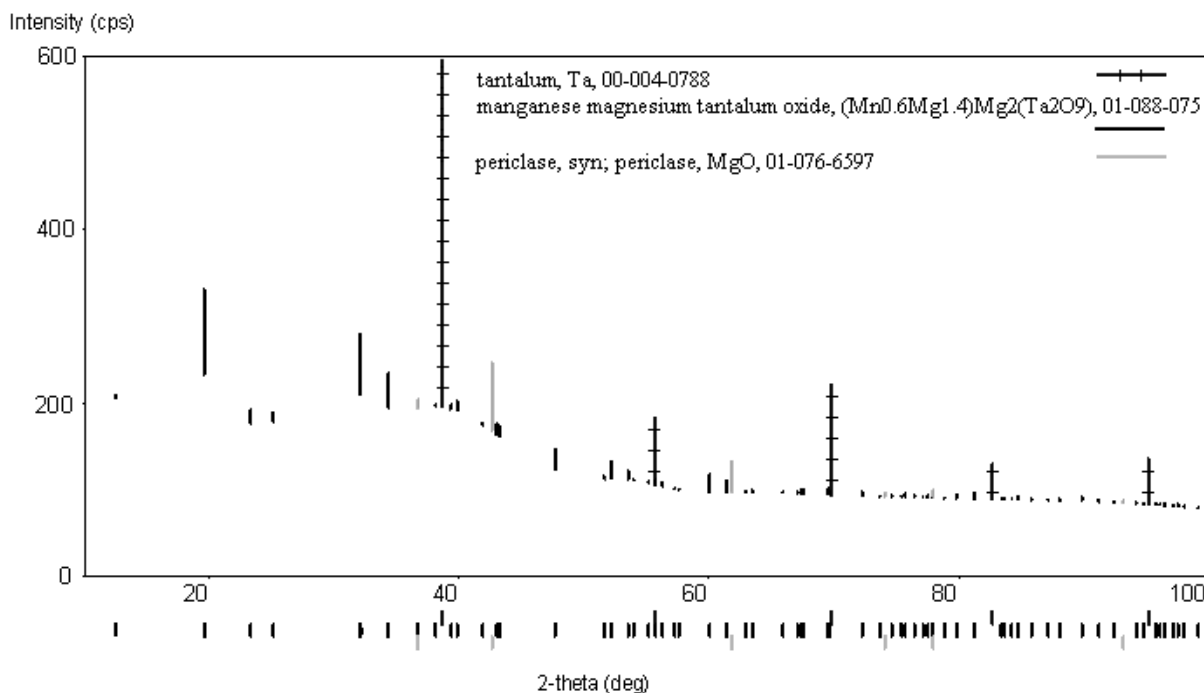**Figure 3.** X-ray diffraction analysis of oxidised anodes

Figure 4. X-ray diffraction analysis of the moulded piece of oxidised anodes with Mg after thermic reduction

3.4 Recycling efficiency of tantalum

Because analysis are without pattern, they do not exclude oxygen in oxidised anodes and reduced moulded pieces. The calculations resulted that in 12 g of oxidised anodes is 1.788 g oxygen and moulded piece with Mg has 1.229 g oxygen. Considering these values, real percentage content Ta in oxidised anodes is equal 81.5% (%$Ta_{oxidisedanodes}$) and in moulded piece with Mg - 77.1% (%Ta_{mp}), of which 38.6% is occur in bounded form, and 61.4% in pure Ta form (%$Ta_{pure,mp}$). Mass of Ta, which is contained in oxidised anodes in then:

$$m_{Ta,oxidised\ anodes} = m_{oxidised\ anodes} \cdot \%Ta_{oxidised\ anodes} = 12.000 \cdot 85.1\% = 10.212\ [g] \qquad (7)$$

Obtained pure Ta in moulded piece with Mg is then:

$$m_{Ta,mp} = m_{mp} \cdot \%Ta_{mp} \cdot \%Ta_{pure,mp} = 12.374 \cdot 77.1\% \cdot 61.4\% = 5.858\ [g] \qquad (8)$$

Recycling efficiency of tantalum can be calculated:

$$\eta_2 = m_{Ta,mp} / m_{Ta,oxidised\ anodes} \cdot 100\% = 5.858 / 10.212 \cdot 100\% = 57.4\% \approx 57\% \qquad (9)$$

4 Discussion and conclusions

The presented method of tantalum recycling from WEEE consists of segregation of tantalum anodes and obtaining pure Ta.

Mechanical treatment by breaking the epoxy resin is an alternative to burning. This operation is effective and easy to implement.

This study has shown the ability and efficiency of leaching of Ag layer counting tantalum anodes by using 8M HNO_3.

Recovery rate of tantalum anodes is at 96%. Such a high rate achieved while maintaining the simplicity of this process.

Impurity, which has failed to get rid in a satisfactory degree, is Mn. It should be investigate the possibility of get rid of MnO_2 layer, for example by several leaching in various and fresh solutions. At each stage of process, remained a part of Mn in material. It proves, than MnO_2 has high resistance to diluted by HNO_3.

Only Mg partially reduced Ta_2O_5 in moulded piece to pure Ta. In this case, recycling efficiency of Ta is estimated at 57%. This value is relatively low, but instead a part of Mg to reduce Ta_2O_5, is formed mixture of Mn and Mg oxides. Therefore, it should be investigate the thermodynamic reasons of this phenomenon.

Oxidised anodes or reduced moulded pieces can be considered as a high content concentrate of Ta (81.5 and 77.1% respectively). However, if the goal is to receive a pure Ta, reduced moulded pieces requires further processing, as it contains reduction by-products, namely oxides of reducing agents. Reduced moulded piece may be dissolved in e.g. HCl, CH_3COOH or diluted aqua regia, which in turn would give pure Ta. Further studies are required.

References

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