MATERIAL CHARACTERISTICS AND RECYCLING OF INDIUM-CONTAINING WASTES

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ABSTRACT

The aim of article is to present the types of indium wastes, including WEEE and by-products resulting from manufacturing. The authors decided to collect information about the chemical composition of wastes containing indium in one place. Methods and processes of recycling indium from WEEE and by-products are also presented.

Keywords: *WEEE, indium wastes, recycling indium*

INTRODUCTION

Indium-containing materials are of various kinds: from minerals and concentrates, metallurgical by-products, to municipal wastes and end-of-life products. Waste of electric and electronic equipment (WEEE) mainly differs in chemical composition and origin. Their indium contents can be as high as 1 wt. %, although often the content is much lower. They can be an alternative source of this critical element next to the primary raw materials. Recycling indium turns out to be very difficult and defined – according to the chemical composition of the initial material.

Due to technological progress, indium occurs more and more often in electrical and electronic equipment, generally in the form of indium-tin oxide. Recycling indium rate is below 1 %, and the main limitation is the high dissipation rate [1].

This article presents the types of indium-containing wastes, their origin and some examples of recycling.

TYPES AND ORIGINS OF INDIUM-CONTAINING WASTES

ITO and etching solution. Pure indium-tin oxide (ITO) is a compound consisting indium and tin oxides in a mass ratio of 9:1; the impurity contents are below 20 ppm [2]. ITO is often admixed to improve functional properties to form a multicomponent mixture comprising also zinc, cadmium, gallium or aluminum. ITO is an optoelectronic material, characterized by transparency in visible light, electrical conductivity and reflects thermal radiation. It is widely used in many optoelectronic devices where transparent conductive layers are required, such as liquid crystal displays (LCD), touch panels, thin film transistors, transparent electrodes, plasma displays, solar cells, multifunctional glasses, anti-frost systems, gas sensors, heat shields and many others. The main manufacturing method of ITO layers with a thickness 1000-3000 angstroms [3] is physical vapor deposition

process by using magnetron sputtering under the influence of direct current on a substrate (glass, ceramics), followed by oxygen plasma oxidation or annealing in an oxygen-free atmosphere [3]. Only 15-33 % of ITO is deposited and the rest 67-85 % is lost as waste that needs to be recycled [2] [4]. Finally, in order to even out the ITO layer, it is etched in a chloride medium [3].

The pattern of ITO layer is usually formed by a photolithography process using acid etching [5]. During etching, tin and indium undergo partial dissolution to form complexes, respectively $[In(H_2O)_6]^{3+}$ and $[SnCl_6]^{2-}$. The etching solution can be used over several etching cycles until in the solution is too high concentrations of impurities [3]. In order to utilization of the spent solution (after ITO etching), it can be neutralized, resulting in the precipitation of the so-called utilization cake in which the indium content may be about 2 % [6].

LCD and photovoltaic cells scraps. An important source of secondary indium is scrap of liquid crystal displays in which the indium is present in the form of ITO on the surface of two glass supports with liquid crystal between them. LCD scrap contains many metals, a small part of which is indium [7] [8]. The situation is similar in the case of photovoltaic cells, especially thin-layer CIS (copper-indium-selenide) solar cells and their modifications: CIGS (copper-indium-gallium-selenide) and CIBS (copper-indium-selenide-boron). Their life span is 25-35 years and the indium content is no more than 2900 ppm [1] [9].

LED. Light-emitting diode (LED) consists of gallium nitride (GaN) diodes which gives high-efficiency white light. LEDs are composed of various semiconductor materials and their key part is a chip which closely adjacent to the metal frame. Chip contains rare and precious metals such as gallium, germanium, arsenic, selenium, indium, gold [10] [11], in the forms for example gallium arsenide (GaAs), gallium nitride (GaN), gallium nitride and indium (InGaN), gallium aluminum arsenide (GaAlAs), zinc selenide (ZnSe), InGaP-Al and germanium [10] [11]. LED lighting has partially replaced traditional light bulb and other types of lighting. Currently, LEDs are starting to be in post-consumer scrap stream [1].

MATERIAL CHARACTERISTICS OF INDIUM WASTES

Tab. 1 shows the chemical compositions of WEEE containing indium. The percentage concentration values of individual elements come from many publications (references in Tab. 1). The materials were divided according to waste types as well as origin and genesis. In WEEE, most indium is in ITO scrap, more than 70 % wt. Apart from relative high concentration of indium in utilization cake, noteworthy there are high concentrations of molybdenum and aluminum. There is also a lot of indium in LCD scrap, about 12 % wt. In photovoltaic cells and LEDs are scarce in indium, and only recycling of indium with other accompanying metals (for example gold and gallium) allows for cost-effective investment.

RECYCLING INDIUM FROM WASTES

ITO [2], spent ITO etching solution [3] [4] [6] [8], as well as LCD scrap [7] [8] [13], photovoltaic cells scrap [9], and ITO-containing scrap in general, are

important sources of secondary indium and other accompanying and valuable elements. Out many of them, a select few are presented below.

ITO and etching solution. In research [2] it was taken into account high tin content in wasted ITO, which should be separated from indium. Recycling tests were carried out in the following order: 1. Leaching, 2. Precipitation of tin sulfide, 3. Indium cementation.

Due to the intensive HCl evaporation and comparable leaching yields with lower H_2SO_4 concentration (compared to the HCl concentration, i.e. 0.75 vs 1.5 M), H_2SO_4 was selected for further tests. The optimal parameters of leaching are as follows: H_2SO_4 concentration – 100 g/l; l/s – 10 ml/g; temperature – 90^0C; duration of leaching – 2 h. With these parameters, In was leached in 99 %, and Sn only in 8 %.

Tab. 1. *Chemical composition of indium-containing wastes (references inside)*

type	source/references		chemical composition											
			Ga	In	Au	Si	Al	Cu	Mo	Sn	Cr	Fe	Zn	Ni
ITO	ITO scrap	[2]	wt. %											
			-	71.21	-	-	-	≤0.01	-	7.65	-	-	-	-
	etching spent sol	[3] [8]	kg/m^3											
			-	~2.1927	-	-	~1.178	~3.249	~0.545	~0.045	-	-	-	-
	etching Utilization[1]	[6]	ppm											
			-	22169	-	340.6	38644.6	1041.1	31418.7	1965.5	9305.7	1421.2	255.5	64.4
LCD scrap		[7]	wt. %											
			-	12.0 (In_2O_3)	-	0.8 (SiO^2)	75.6 (Al_2O_3)	0.2 (CuO)	-	1.6 (SnO_2)	1.0 (Cr_2O_3)	4.5 (Fe_2O_3)	0.8	0.4 (NiO)
photovoltaic cells	CIS	[12]	wt. %											
			-	0.04 ($CuInS_2$)	-	96.9 (glass)	-	-	0.025	-	-	-	0.035 (ZnO)	0.0003
LED	chips	[10]	ppm											
			5377.0	551.0	1521.8	-	-	-	-	-	-	-	-	-
	waste		~36.20	~1.56	~16.66	5.31	2.27	-	-	-	-	-	-	-

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Tin precipitation was carried out from post-leaching solution by using H_2S. The precipitation reaction is very fast - less than 10 minutes. Due to a certain SnS solubility, totally tin precipitation cannot be obtained. Further selection of parameters was aimed at minimizing the loss of co-precipitated indium. The effect of the initial acidity shows that the tin precipitation yield is proportional to the indium loss. Tin precipitation yield and indium losses increase as temperature decreases. The optimal conditions for tin removal are as follows: 1 M initial acidity and temperature 50^0C. Tin precipitation yield was almost 100 % and the indium

loss was only 0.47 %. The precipitate consists of tin oxide and sulfide as well as traces of indium in the form of oxide and sulfide.

From the purified solution, indium was precipitated by cementation with zinc under the conditions: 65^0C, pH = 1-1.5, 40 h. During cementation, the solution was neutralized with Na_2CO_3 to pH = 1.2. The cementation yield was 99.9 %.

The cemented indium was pressed into pellets, covered with NaOH in the amount of 50 % by weight of indium and melted at 300^0C for 3 hours. Finally, indium with a purity of 99.92 % was obtained.

Study [3] was concerned the recycling indium from spent etching solution. Proposed method was aimed at recycling not only indium, but also Mo, Sn and Al. Firstly, Mo and Sn are removed from spent solution by solvent extraction with Cyanex 272, then proper indium extraction is performed on the purified solution with DP-8R. The remaining components of solution, such as Cu or Al, are recovered by cementation or neutralization after indium extraction.

Indium solvent extraction from Mo-Sn-free solution, with an aqueous to organic phase ratio <10:1, was performed at a controlled pH = 0.7. The optimal concentration of DP-8R is 0.5 M, which allows the extraction of most indium. Then, re-extraction with 4 M HCl was carried out for 4-5 minutes at a 10:1 ratio of organic to aqueous phase. After re-extraction, the indium was concentrated 28-fold. Finally, indium is recovered strictly by a hydrometallurgical route until the indium sponge is obtained.

Other study [6] concerned the recycling indium from utilization cake. Due to the chemical composition of utilization cake, which contain some admixtures, laboratory tests on the recycling indium was carried out in the following order: 1. Alkaline leaching, 2. Acid leaching, 3. Indium solvent extraction, 4. Indium electrolysis.

In the alkaline leaching of utilization cake, impurities such as Mo, Al, Cr and Mg are removed. Among the various reagents, NaOH is selected as the one which can remove the above-mentioned impurities. Overall, about 70 % of impurities was removed by using 12 M NaOH. As a result, indium concentration in the solid increase to 41.1 %.

For indium solvent extraction is needed to indium leaching. Hence, the solid residue from alkaline leaching was taken up in 0.3 M HCl in such an amount that the impurities were dissolved into their corresponding chloride forms, i.e. 130 % based on the stoichiometry. Indium extraction was carried out with pure PC88A and saponified by NaOH. Regardless of the degree of saponification, indium extraction yields were almost 100 %. On the other hand, the degree of saponification affects the impurities co-extraction yields, e.g. pure PC88A co-extracts Fe, Mo and Sn, and saponified PC88A – Cu, Al, Na, Cr and others. Generally, a more optimal option is to use unsaponified PC88A. It is not possible to extract indium selectively without co-extracting the impurities, and the extraction should be carried out with as little adicification as possible. At optimal parameters, which are ratio of organic to aqueous phase is 3:1 for 5 min, the indium extraction yield was up to 98 % and

along with indium, mainly Mo, Fe and Sn are co-extracted. Indium re-extraction was carried out with the use mineral acid, whereby, regardless of the acid, the concentration of hydrogen ions is important, which should be at least 1 M. Finally, at 2 M concentration, indium solution is obtained, mainly contaminated with Fe.

The last step is the indium electrolysis. Due to the high purity of the indium electrolyte (>99.5 %), the electrolysis can be carried out without a diaphragm. Obtained electrolytic indium purity is 99.997 %.

Photovoltaic cells scraps. In fact, there are only a few industrial recycling indium processed from thin photovoltaic cells, consisting of mechanical-chemical treatment - SENSE and wet mechanical treatment – RESOLVED [14]. Depending on the type of cell modules, several strategies are distinguished [9] [14]: CIGS – waterjet cutting and chemical treatment; CIS, CIGS and CdTe – pyrolysis and chemical treatment; Si – grinding and pneumatic separation. RESOLVED, compared to SENSE, requires less chemicals and generates less wastes. The process that was the subject of the research on indium recovery from photovoltaic panels modules containing CIS and CdTe [9] consists of several stages: 1. Thermal disassembly, 2. Grinding, 3. Separation of semiconductor material from glass, 4. Flotation.

Gradual heating of photovoltaic panels modules with a size of 10x10 or 30x30 cm^2 to temperature 500^0C causes the laminate to be disassembled. The protective glass is separated and the support glass with a semiconductor (including indium) on its surface is further mechanical processing.

Grinding is a necessary process step in order to provide sufficient material for subsequent stages. The grain size must be small enough (less than 20 mm) for them quick and complete sandblasting or exfoliation of support glass during further wet mechanical processing. Photovoltaic panel modules containing CIS were processed in a rotary cutter and impact mill.

The separation of the semiconductor material from glass was carried out in two ways: either by sandblasting or by exfoliation. Sandblastings with glass beads, ZrO, Al_2O_3 and Fe were most effective in separating. Wet exfoliation runs at an average water content of 11.8 % by 30 min and the rotational speed of the mill and agitator 900 and 25 rpm, respectively. After exfoliation, the mixture of glass, semiconductor material and plastics was rinsed and sieved. Fraction <150 μm contains 2010 mg of indium per 1 kg.

Flotation of the fraction rich in CIS semiconductor material was performed most efficiently with KAX (potassium amyloxentogenate). By flotation process, which technological conditions were: mixing speed 1000-1500 rpm, air stream 150 l/h, KAX concentration 0.5-1 g/kg; even a 25-fold enrichment of indium was achieved [9]. Complete CIS separation in only possible by chemical treatment, during which the residual glass can be easily removed.

LED. Currently, several technological processes have been developed for the LED recycling. The vast majority of them are based on hydrometallurgy, mainly due to the very low concentrations of metals. They are focuses on gallium recovery. Only a few others take into account the indium co-recovery [10] [11] [15].

The research [10] concerned the indium and gallium recycling from LED diodes scrap by pyrolysis and mechanical processing. This method is based on the vacuum pyrolysis of gallium and indium nitrides contained in LEDs. As a result of pyrolysis and condensation, an organic fraction and a metallic condensate/solid residue are obtained. The latter is enriched by grinding and sieve separation. In this way, carbon, wires and metal frames are separated from the main product, which is a concentrate rich in rare metals. Main product is vacuum evaporated to rectify a fraction, one of which is a gallium and indium concentrate.

Vacuum pyrolysis was carried at temperature 500^0C. The metallic condensates containing Ga-In and Au were condensed in the temperature range 324-802 and above 802^0C, respectively. Since the pyrolysis temperature was lower than the metals condensation temperatures under vacuum conditions, the metals were remained in the solid residue, which was the material for the next stage of enrichment. At pyrolysis temperature, the weight loss was 57 wt. %.

The solid residue from the vacuum pyrolysis was ground and sieved on 18 mesh screen. Subsieve fraction was coal scrap. Oversieve fraction was ground and sieved though 40 mesh screen. The oversieve fraction was a concentrate rich in rare metals.

This concentrate was subjected to vacuum pyrolysis at the temperature 1100^0C for 60 min. Two condensates were obtained. Ga-In-bearing concentrate has lower condensation temperature. Along with Au, Cu was also subject to condensation in the zone of the highest temperature. Ga, Au and In recovery yields were about 93.5, 95.7 and 31.6 %, respectively.

In other study [15], which also aimed at recycling indium from LEDs scrap, were carried out in following order: 1. Alkalizing roasting, 2. Leaching. The purpose of roasting was to bring the Ga and In from the hard- to easy-leachable form.

During alkalizing roasting, wherein the alkalization agent was Na_2CO_3, the following reactions proceed:

$$4GaN_s + 3O_{2_g} \xrightarrow{\Delta T} 2Ga_2O_{3_s} + 2N_{2_g} \quad (1)$$

$$4GaN_s + 2Na_2CO_{3_s} \xrightarrow{\Delta T} 2NaGaO_{2_s} + CO_{2_g} + N_{2_g} \quad (2)$$

LED scrap roasting was carried out in the following conditions: 900^0C, 3 hours and the ratio of LED scrap to Na_2CO_3 was 1:1 (wt.).

Then, the calcined LED scrap was leached by using HCl. Leaching yields of gallium and indium significantly increase as acid concentration increases from 1 to 2 M, and a further concentration increasing does not affect efficiencies. The ratio of liquid to solid phase plays an important role during leaching. Leaching yields significantly increase with an increase l/s ratio from 10 to 30 ml/g, from 63 and 61 to 91 and 93 % for gallium and indium, respectively. Similarly, leaching duration has a important impact on the leaching yields. The greatest leaching yields occurred with increasing the duration from 16 to 32 min.

CONCLUSIONS

WEEE and manufacturing wastes are an important source of secondary indium. Contained indium in them is primarily in ITO form. Talking about ITO wastes, it should also consider spent etching solution and utilization cake. Recycling indium method is selected individually depending on the type and form (solid or liquid phase) of the scrap and by-product. Recycling indium methods are both pyro- and hydrometallurgical, or a combination of them. Often for technological and economical reasons, indium is one of many elements (for example gallium and gold) recovered from WEEE.

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