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PRELIMINARY STUDIES ON SIMULTANEOUS RECOVERY OF PRECIOUS METALS FROM DIFFERENT WASTE MATERIALS BY PYROMETALLURGICAL METHOD

WSTĘPNE BADANIA JEDNOCZESNEGO ODZYSKU METALI SZLACHETNYCH, Z RÓŻNYCH MATERIAŁÓW ODPADOWYCH, METODĄ POROMETALURGICZNĄ

Automotive catalytic converters have a limited life time, after which the catalyst must be replaced or regenerated. The spent catalytic converters contain small amount of precious metals. Recovery of these metals is essential for environmental and economic reasons. The waste electronic equipment is also an attractive source for recovery of precious metals. Precious metals in electronic scraps are concentrated mainly in printed circuits and integrated circuits – so generally in elements that are the most diverse in their composition. Material heterogeneity of these elements is the reason why there is no universal method for processing this type of scrap. Methods used in the world for recovery of precious metals from spent auto catalytic coverters and electronic wastes by pyrometallurgical and hydrometallurgical methods were mentioned in this paper. The results of simultaneous melting of electronic waste with spent automotive catalysts were presented. The printed circuit boards were used as the carrier and as a source of copper. The precious metals present in the catalyst were collected in copper.

Keywords: electronic waste, copper, platinum, metal collector, pyrometallurgical methods

Samochodowe konwertory katalityczne mają ograniczony czas życia, po czym katalizator ten należy wymienić lub poddać regeneracji. Zużyte katalizatory zawierają niewielkie ilości metali szlachetnych, a możliwość odzysku tych metali jest istotna ze względów ekonomicznych i ekologicznych. Równie atrakcyjne źródło metali szlachetnych stanowi wycofany sprzęt elektroniczny. Metale szlachetne w płytkach elektronicznych są zlokalizowane głównie w obwodach drukowanych układów scalonych, które są najbardziej zróżnicowane pod względem składu. Niejednorodność materiałowa tych elementów powoduje, że nie ma uniwersalnego sposobu przetwarzania tego rodzaju złomu. W artykule zwrócono uwagę na metody pirometalurgiczne i hydrometalurgiczne stosowane na świecie do odzysku metali szlachetnych ze zużytych katalizatorów samochodowych oraz odpadów elektronicznych. Przedstawiono wyniki badań próby wspólnego przetopu odpadów elektronicznych z odpadami zużytych katalizatorów samochodowych. Odpady elektroniczne w postaci drukowanych płytek obwodowych zostały wykorzystane jako nośnik i główne źródło miedzi, metalu pełniącego rolę metalu zbieracza platynowców, obecnych w katalizatorach. Otrzymano stop Cu-Fe-Au-Pt odzyskując w ten sposób platynę na poziomie około 78%.

1. Introduction

Today almost half of the produced platinum, the majority of palladium and 80% of rhodium is used for the production of auto catalytic converters. Catalytic converters have a limited life time (about 80 000 km), after which the catalyst must be replaced or regenerated. Large quantities of used catalytic converters give possibility to recover the considerable amount of platinum. Possibility of reusing the material, that is platinum group metals recovery from used auto catalytic converters, becomes very important, taking into consideration the economical management of natural resources and energy.

Catalytic converter is built from stainless steel shell with a ceramic or metallic carrier inside it. Ceramic carrier is made from alumina with a small addition of cerium oxide. The ceramic carrier is then covered by a thin layer of precious metals such as: platinum, palladium and rhodium (PGMs – Platinum Group Metals). These metals play a catalytic role [1]. To recover precious metals from spent catalysts many hydro- and pyrometallurgical methods are used [2]. None of these methods however, is perfect and can be used to recover metals from all types of spent catalysts. In the hydrometallurgical methods PGMs contained in the used auto catalytic converters are dissolved in an aqueous solution of chlorate, perchloric acid, Cl_2, H_2O_2, bromate, nitrate, aqua regia or cyanide solution [3-5]. The obtained solutions contain PGMs, but their concentration is low. So the next stage is to concentrate the solutions and extract metals from these solutions [6]. The hydrometallurgical methods also require to solve the problem of harmful waste solutions generated during the process.

In pyrometallurgical methods grinded carriers covered by the PGMs are melted with the addition of other metal

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which has a special function – a metal collector. The main advantages of applying metal collector is to decrease the temperature of the process, and in the same time to reduce the cost of the PGMs recovery. Melting of typical ceramic carrier (silicon-aluminium-magnesium oxide) requires high temperature and addition of fluxes. The operating temperature of common processes is between 1500°C and 1900°C [5,7]. Obtained alloy is rich in PGMs, so the next stage is the PGMs purification. Different metals such as calcium, zinc, magnesium, cadmium, lead, nickel and copper can be used as a metal collector. These metals are selected taking into account the solubility of platinum [1,6,7]. Unfortunately there are some disadvantages: pyrometallurgical methods require special equipment which allows to reach the desired temperature; it is not only expensive but also highly energy consuming as well. The methods used in the world for the recovery of PGMs from spent auto catalytic converters are shown in Fig. 1.

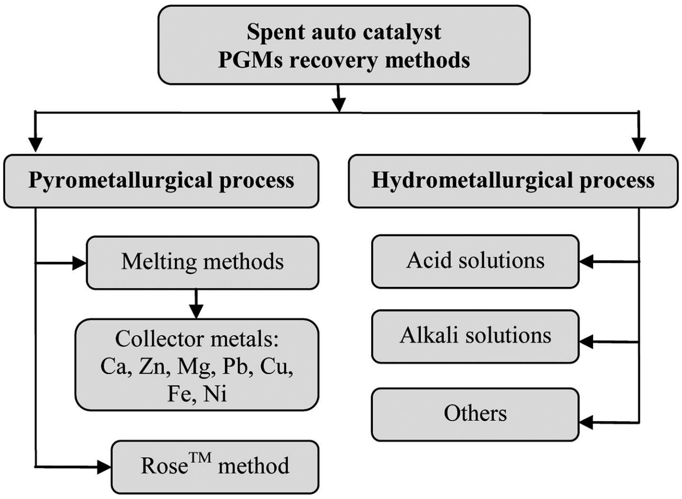

Fig. 1. Applied methods of PGMs recovery from spent auto catalysts

Systematic works on the possibility of using metal collectors for the recovery of platinum from auto catalysts are carried out in the Division of Extractive Metallurgy and Foundry of Silesian University of Technology. These works include experiments applying innovative solutions for platinum elution from the surface of a catalyst, using magnetohydrodynamic pump and lead as a metal collector [8]. In this method the metal collector is used, the main aim of which is to capture platinum. In case of PGMs recovery from used auto catalytic converters the main problem is the efficiency of PGMs elution from catalytic carriers. Single flushing of the catalytic carrier with liquid metal allows to recover only some part of metals. Additionally, if the level of PGMs is low in single catalytic carrier, the process seems to be unprofitable. Much better results can be obtained if the multiple flushing is used. The best solution in this case could be applying the continuous flushing with liquid metal and placing catalytic converters carriers in this flux [8]. The research using copper as metal collector (Cu of M0B species with the purity 99,99%) was also carried out [1].

For the recovery of precious metals from electronic scrap, conventional pyrometallurgical processes are successfully used. An example can be Umicore company in Belgium, conducting highly-efficient processing of different fractions of electronic waste. Umicore recovers precious metals such as gold, silver, platinum group metals (Pd, Pt, Rh, Ir, Ru) and a number of other metals [9]. In addition to well-known methods for the recovery of precious metals from electronic scrap by pyro- or hydrometallurgical processes, new solutions that could replace or improve current practice are sought. Much attention is devoted to wet methods, aiming to develop more environmentally friendly techniques, taking into account the biohydrometallurgical methods [10-13].

In the study the case of simultaneous melting of electronic waste (in the form of a PCBs) with spent catalysts have been analysed. Printed circuit boards are the main carrier of valuable metals in the electronic waste. Generally PCBs scraps contain approximately 40% of metals, 30% of plastics and 30% of ceramics [14]. Typical metals content in PCBs of mobile phones is following: 10-20% of copper, 1-5% of lead, 1-3% of nickel, about 0.3-0.4% of Ag, Au and Pt, the rest is glass and ceramics. However given values may vary depending of PCBs age and manufacturer. The economical value of electronic scraps is determined by precious metals content which are gold, silver, palladium, and copper. However among these metals, copper is a dominant component of PCBs and in fact, this metal is the most interesting and it can be use as a secondary raw material [15-18]. The aim of the study was to determine the applicability of electronic waste (in the form of PCBs) as a carrier and a major source of copper – the metal that acts as a metal-collector of platinum in the case of spent auto catalysts.

2. Experimental method

Research was conducted on the waste material in the form of:

- carriers of spent auto catalysts (AC) coming from different cars and
- printed circuit boards (PCBs) obtained from used mobile phones.

The scraps of PCBs and auto catalyst were ground to powder by using cutting mill. Then they were melted in electric inductive furnace (type St 5/40) for one hour in 1700°C. The samples in the amount of 100 g (ratio of 4:1 PCBs:AC) were melted with addition of fluxes. The main aim of this stage was to collect platinum in copper derived from PCBs. The analysis of metals content in the samples were carried out by means of the atomic adsorption spectrophotometer (SOLAAR M6-UNICAM Atomic Absorption). The platinum average content in ceramic carriers was between 0.11% and 0.13% whereas PCBs contained Cu 30.22%, Fe 1.91%, Au 0.12%, Zn 0.24%, Sn 0.94%.

The surface of the samples (before and after melting process) was analysed by using a scanning electron microscope (SEM), equipped with a Hitachi S 4200. Microanalysis of the chemical composition was performed by EDS method (Energy Dispersive Spectrum) [19]. Observation of the surface and the X-ray microanalysis were carried out at an accelerating voltage of 15kV. Results of AC and PCBs microanalysis and their chemical composition were shown respectively in Fig. 2 and Fig. 3.

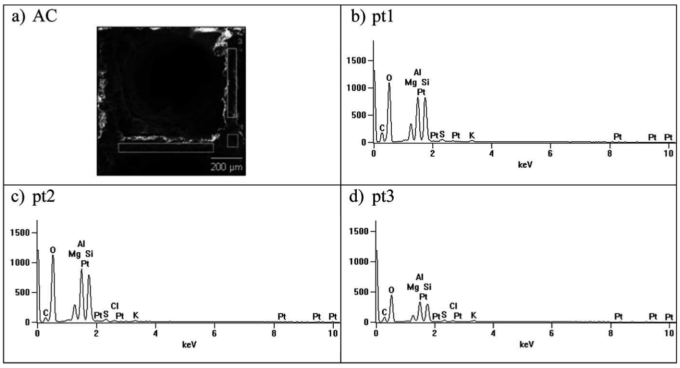

Fig. 2. SEM microphotograph of AC surface (a) and microanalysis of chemical composition in marked areas: pt1 – pt3 (b-d)

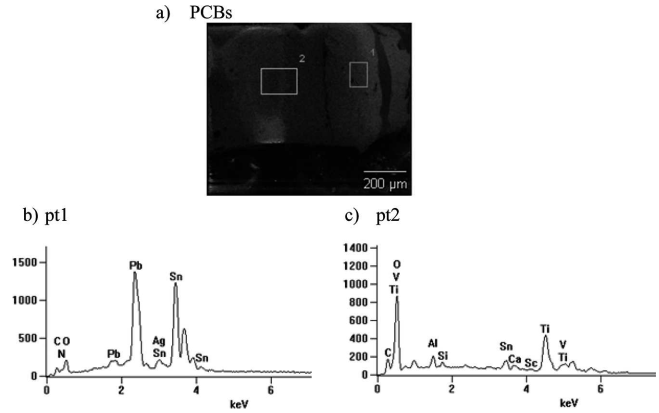

Fig. 3. SEM microphotograph of PCBs surface (a) and microanalysis of chemical composition in marked areas: pt1 and pt2 (b, c)

3. Results

As a results of melting, the alloy of Cu-Fe-Au-Pt and slag were obtained. Table 1 shows the chemical composition of such alloy. Definitely the dominant metal is copper with the addition of platinum and gold. The alloy contains also about 5% of iron and about 2% of tin. The results of microscope observations and chemical composition analysis by SEM are shown in Figure 4 and 5 and summarized in Table 2. Microscope studies indicate the complex structure of the alloy. Copper and platinum are present in the microregions in significant different mass ratio. These metals were accompanied by metals derived particularly from the PCBs (Ni, Sn). Carbon and silicon (components of spent catalysts as well as partially of PCBs) were also present in the surface of alloy. The average recovery level of metals is following: Pt 78.3%, Cu 81.2%, Au 83.7% Fe 60.6%. During melting process average – 37% loss of weight was observed, mostly related to the incineration of organic and plastics components in PCBs. Formed slag, next to typical oxide constituents, contained also copper (from 0.31% to 0.66%). In case of properly conducted process, there should not be any copper and precious metals in the slag. For greater efficiency and purity of the alloy, it is necessary to correct the process conditions. Proposed procedure that improves its purity may be refining, adapted to local conditions [20,21].

TABLE 1

Chemical composition of received Cu-Fe-Au-Pt alloy

Sample	Alloy mass, g	Concentration, %				
		Cu	Pt	Au	Fe	Sn
1	14.74	75.461	0.640	0.271	4.984	2.301
2	12.98	69.198	0.680	0.150	5.866	2.076
3	12.34	70.766	0.855	0.162	4.280	1.374

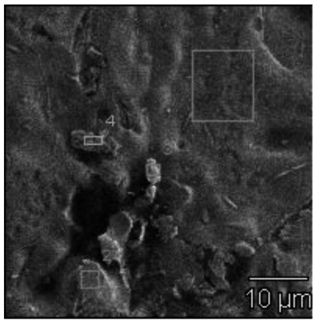

Fig. 4. Structure of alloy with marked selected areas for X-ray energy spectra (pt1 – pt4)

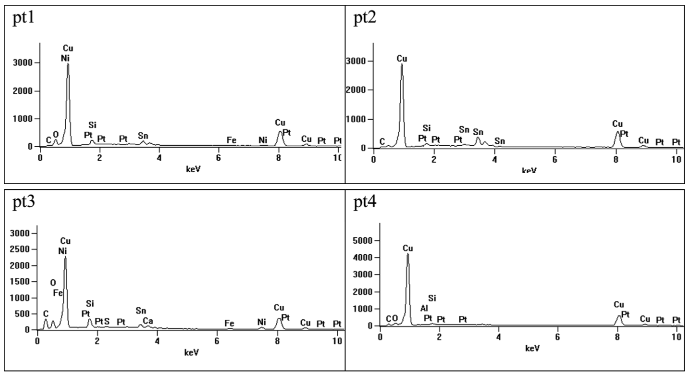

Fig. 5. Microanalysis of the chemical composition by EDS method (pt1-pt4)

TABLE 2

Chemical composition of Cu-Fe-Au-Pt alloy in places marked in Fig. 4

Analysis, No.	Content, % mas.									
	C	Al	Si	S	Ca	Fe	Ni	Cu	Sn	Pt
pt1	3.62	-	2.43	-	-	0.97	2.64	76.51	6.63	0.01
pt2	1.52	-	1.47	-	-	-	-	80.37	16.27	0.37
pt3	22.80	-	3.42	0.34	0.34	0.97	2.64	52.91	4.27	0.31
pt4	6.39	0.31	0.59	-	-	-	-	89.30	6.63	0.13

4. Conclusion

Spent automotive catalysts and printed circuit boards are a rich source of PGMs. Due to high value of PGMs, the recycling of the spent catalysts or e-waste at the end of their life is crucial for economic or environmental reasons. Such an approach gives considerable benefits such as limiting the number of waste disposal, saving natural resources, limiting the electricity consumption and diminishing pollutant emission. As a result of simultaneous melting of spent catalysts with PCBs, Cu-Fe-Pt-Au alloy was obtained. As a metal-collector, copper derived from PCBs was used and additionally Fe played the role of a collector. During the melting process about 78% of platinum went to copper. Organic and plastics components of PCBs were incinerated during melting process and ceramic carrier created the slag. The ef?ciency of recovering platinum is promising. However, it is necessary to improve process conditions.

REFERENCES

[1] A. Fornalczyk, M. Saternus, Platinum recovery from used auto catalytic converters in electrorefining process, Metalurgija **52**, 2, 219 (2013).

[2] J.S. Yoo, Metal recovery and rejuvenation of metal-loaded spent catalyst, Catalyst Today **44**, 27-46 (1998).

[3] Manis Kumar Jha, Jae-Chun Lee, Min-Seuk Kim, Jinki Jeong, Byung-Su Kim, Vinay Kumar, Hydrometallurgical recovery/recycling of platinum by the leaching of spent catalysts: A review, Hydrometallurgy **133**, 23 (2013).

[4] B. Pospiech, Studies on platinum recovery from solutions after leaching of spent catalysts by solvent extraction, Physicochem. Probl. Miner. Process **48**, 1, 239 (2012).

[5] R. Rumpold, J. Antrekowitsch, Recycling of platinum group metals from automotive catalysts by an acidic leaching process, The Southern African Institute of Mining and Metallurgy, Platinum 2012, 695.

[6] Byung-Su Kim, Jae-chun Lee, Seung-Pil Seo, Young-Koo Park, Hong Yong Sohn, A Process for Extracting Precious Metals from Spent Printed Circuit Boards and Automobile Catalysts, Journal of Metal **56**(12), 55 (2004).

[7] A. Fornalczyk, M. Saternus, Vapour treatment method against other pyro- and hydrometallurgical processes applied to recover platinum from used auto catalytic converters, Acta Metall. Sin **26** (3), 247 (2013).

[8] A. Fornalczyk, S. Golak, M. Saternus, Mathematical Prob. in Engineering, Article ID 461085, doi:10.1155/2013/461085 (2013).

[9] Ch. Hagelüken, M. Verhelst, Recycling of precious metals catalysts, Petroleum Technology Quarterly **9**, 21 (2004).

[10] J. Willner, A. Fornalczyk, Electronic scraps as a source of precious metals, Przemysl Chemiczny **9**(4), 517 (2012).

[11] J. Willner, A. Fornalczyk, Extraction of metals from electronic waste by bacterial leaching, Environment Protection Engineering **1**, 197 (2013).

[12] Tao Yang, Zheng Xu, Jiankang Wen, Limei Yang, Factors influencing bioleaching copper from waste printed circuit boards by Acidithiobacillus ferrooxidans, Hydrometallurgy **97** (1-2), 29 (2009).

[13] S. Ilyas, Ch. Ruan, H.N. Bhatti, M.A. Ghauri, M.A. Anwar, Column bioleaching of metals from electronic scrap, Hydrometallurgy **101** (3-4), 135 (2010).

[14] H.M. Veit, A.M. Bernardes, J.Z. Ferreira, J.A.S. Tenorio, C.F. Malfatti, Recovery of copper from printed circuit board scraps by mechanical processing and electrometallurgy, Journal of Hazardous Materials **B137**, 1704 (2006).

[15] C. Ludwig, S. Hellweg, S. Stucki, Municipal Solid Waste Management: Strategies and Technologies for Sustainable Solutions, Springer, Berlin-Heidelberg-New York, 2003.

[16] Maria Paola Luda, Recycling of Printed Circuit Boards Integrated Waste Management – Volume II, p.285 Edited by Er. Sunil Kumar, 2011.

[17] Y. Chehade, A. Siddique, H. Alayan, N. Sadasivam, S. Nusri, T. Ibrahim, Recovery of gold, silver, palladium, and copper from waste printed circuit boards, International Conference on Chemical, Civil and Environment Engineering (ICCEE'2012) March 24-25, 2012 Dubai.

[18] M. Buchert, A. Manhart, D. Bleher, D. Pingel, Recycling critical raw materials from waste electronic equipment, Oeko-Institut e.V., Germany, Darmstadt, 24.02.2012.

[19] J. Cebulski, J. Barcik, Plastify of alloy based on the matrix of intermetalic FeAl phase, Archives of Metallurgy **45**(3), 315 (2000).

[20] K. Janiszewski, K. Refining, of liquid steel in a tundish using the method of filtration during its casting in the CC machine Archives of Metallurgy and Materials **58**, 2, 513 (2013).

[21] S.Z. Ivanovic, V.K. Trujuc, M.D. Gorgievski, L.D. Misic, D.S. Bozic, Removal of platinum group metals (PGMs) from the spent automobile catalyst by the pyrometallurgical process, 15th International Research/Expert Conference, TMT 2011, Prague, Czech Republic, 12-18 September 2011.

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