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ECO-FRIENDLY RECYCLING POTENTIAL OF MICROWAVE MELTING FOR THE RECOVERY OF USEFUL AND PRECIOUS METALS FROM E-WASTE

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ABSTRACT. The processing of waste electrical and electronic equipment (WEEE) has become an issue of significant importance due to the large volumes being generated and to the content of rare and valuable metals as well as environmentally toxic materials (organic compounds). Presently, WEEE is regarded as an important secondary resource of useful metals.

The aim of this study is to evaluate the content of base and precious non-ferrous metals in such wastes collected in Romania and to assess the potential of their recycling through processing in microwave field.

Electric and electronic wastes are complex mixtures of materials and components, with chemical compositions which depend on their sources (printed circuit boards - PCBs, mobile phones, television and radio sets, home appliances and industrial equipment). In PCBs the metallic fraction is of approximately 30-50 wt.% (with 45-65 wt.% Cu, 0.5-20% Pb, 15-25% Sn, 5-8% Zn, 0.4-0.8% Ag, 0.08-0.2% Au and 2-5% other metals such as Fe, Ni, Al, Sb, Cr, Mn etc.). The non-metallic fractions, which account for 50-70 wt.%, contain substances such as brominated flame retardant,

thermosetting resin, reinforced materials and other toxic and hazardous organic compounds. The combustion of these materials during the pyrometallurgical processes may cause serious environmental problems, due to the generation of toxic gases.
The microwave melting of WEEE represents a promising state-of-the-art, ecological and energy efficient alternative for the conventional methods with a remarkable applicative potential. The advantages of this method are: ***i.*** reduced melting time with energy savings of 30-40%, compared to traditional processes (a microwave furnace can easily attain temperatures up to 1600°C in less than 30 minutes); ***ii.*** low content of organic substances. ***iii.*** facile extraction of the enclosed metal fractions; ***iv.*** improved process control; ***v.*** absence of direct contact with the melting materials and ***vi.*** environmental-friendly approach through the possibility of treating the toxic gas emissions in a microwave field at high temperatures (1300 ÷ 1400^{0}C).

Key words: *recycling, non-ferrous metals, microwaves, e-wastes*

INTRODUCTION

In the economy of today the production of metals has heavily increased in order to meet the need of metals for a wider range of applications. The development of the industry in general and particularly of the metallurgical industry is conditioned by the solution of major issues, which ensue the relation between the industry and nature, strictly oriented towards the protection of natural and energy resources and pollution control. Currently, the source of metals has shifted from highly concentrated ores to ores with low concentrations and various industrial wastes (Grundas, 2011). Although the practice of recovering valuable metals has been applied for a long time, today the protection of natural resources and of the environment is a significant incentive for the recovery of metals after use.

The concerns about the conformation to the legislation regarding environment protection and the necessity to harmonize the processes and the technological progress and the sound management of raw materials and energy resources must lead to the exploitation of wastes by technologies which offer the optimum solution, both economically and environmentally. The collection, recycling and processing of wastes represent a priority which is found in the commitments assumed by Romania towards the European Union. In Romania, waste deposits are amongst the sources which generate impact and risk for human health and for the environment, as a result of a lack of facilities and insufficient exploitation.

Apart from the primary obtaining of non-ferrous metals from ores, a process which requires high energy consumption, recycling is gaining an increasing importance. Recycling constitutes a major component in the replacing of the ores for several metals. The demand for metallic wastes depends on the structure of the industry and on the availability of waste processing technologies for obtaining products with high added value. The goals of the development strategies for various industrial domains are encompassed in two directions:

- the development of state-of-the-art technologies which significantly reduce emissions;
- the increase of recycling and recovery efficiencies to values close to 100% for byproducts.

The metallic wastes can be recovered from a wide range of products which are at the end of their lifecycle, rejects or metallic scraps resulting from machining. Beside the base metal, some metallic wastes also contain other metals such as: zirconium, tungsten or precious metals. Thus, copper, aluminum, lead, zinc, precious and refractory metals, as well as other metals, can be recovered from products or their residues and can be reintroduced in the economic cycle by recycling. Through processing wastes are transformed in secondary raw materials. The introduction of a higher proportion of secondary raw materials in the production processes leads to the substantial reduction of ore and energy consumptions (IPPC, 2001), thus contributing to the increase of the industrial profitability (www.cee-environmental.com, Resource Recycling Fund Management Committee, Govt moves to stem tide of 'e-waste').

The energy saving is so high that it is possible to also re-melt economically the wastes with a low metal content, as well as impure and coated wastes (plated or coated parts, burnt or etched wires). The production of secondary nonferrous metals consumes a much lower quantity of energy, compared to the winning of primary metal from the ore (table 1).

Table 1. *Energy and materials savings in non-ferrous metals recycling*

Recycled metal	Percent of recycled metal used in obtaining new metal	Energy savings
Aluminum	39 %	95 %
Copper	32 %	85 %
Lead	74 %	60 %
Zinc	20 %	60 %

The value of the recycled non-ferrous metals is very high, for copper representing approximately 95% of the value of the primary metal extracted from the ore. The recycling rates of nonferrous metals are significant, with values starting from 67% and up to 92% in the automotive industry, constructions, electronics and packaging.

Another major advantage of recycling non-ferrous metals from wastes is the reduction of the CO_2 emissions produced during the processes of obtaining primary metals. Recent EU data state that the use of recycled raw materials, including metals, leads to the reduction of CO_2 emissions with approximately 200 de million tons/year. In the case of copper recycling, the CO_2 emissions are reduced with almost 65%, and in the case of lead the reduction is of approx. 99%.

The electronic products waste also contains valuable secondary materials - metals and plastics – which can be used in the manufacturing of new products. Approximately 25% of the annual Ag and Au production and 65% of the Pd and Pt production come from recycled materials (WEEE[1] and catalyzers), (*Sustainable Innovation and Technology Transfer Industrial Sector Studies, Recycling – from E-Waste to Resources*, 2009*)*. The necessity of WEEE processing results from the large quantities generated and the content of valuable metals (0.1 % Au, 0.2 % Ag, 20 % Cu, 4 % Sn-figure 1) (*Recycling technology advances and new material development key to successful e-waste recovery, Integrated Approach to Electronic Waste (WEEE) Recycling, 2007*). It is estimated that approximately 20 ÷ 25 Mtons/year of electronic wastes are generated globally, the largest

[1] WEEE – electric and electronic equipment waste

quantities being produced in Europe, USA and Australia (Havlik et al., 2009; Robinson, 2009). In the EU, approx. 6.5 ÷ 7.5 Mtons WEEE/year are generated, representing 16 Kg/inhabitant. The WEEE[2] composition is presented in figure 1.

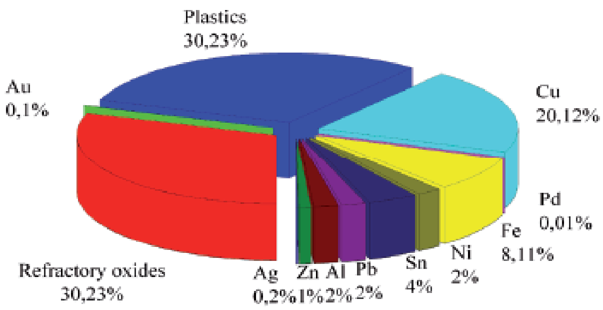

Fig. 1. *WEEE composition*

Generally, the process of recycling non-ferrous metals implies several steps, such as: sorting, shredding, pressing and melting the wastes in various types of furnaces. The resulting alloys are cast in the shape of slabs or ingots and are used directly in the metallurgical industry or they can be transformed in metal sheet or other products.

Depending on materials, various types of equipments are used for melting the secondary non-ferrous metals. For this purpose, the selection of the optimum melting method is determined by the metallic component of the waste, the waste geometry, the waste composition and by the manner of operating the furnace. For the oxide-poor wastes or with organic impurities, the adequate melting equipment is the hearth furnace, with no salts addition. The large sized wastes are melted in crucible or double chamber furnaces. Even scrapings can be melted with high extraction efficiency in hearth furnaces. The metal extraction efficiency is the main productivity criterion of waste melting.

[2] *An Integrated Approach to Electronic Waste (WEEE) Recycling*, Project funded by DEFRA Waste and Resources Research Programme Reference WRT208, Final Project Report, Deliverable M12 SID5 Form – Section 8, 2007

USING MICROWAVE ENERGY FOR MELTING NONFERROUS METAL WASTES

The pyrometallurgical process represents a common solution for recovering valuable elements from various industrial wastes. However, these conventional pyrometallurgical recycling processes (e.g. the Waelz process) present some inherent drawbacks.

The use of microwaves (MW) for heating originated in 1946 and has been applied in various fields (Grundas, 2011). Recently, researchers investigated the microwave heating process as a promising recycling method, since it presents characteristics such as a fast heating rate and direct internal heating. Microwave heating can also provide significant time and energy savings.

Until recently, metal heating was not a major application field of microwave energy. It is well known that while a bulk metal reflects microwaves, metal particles and thin films can be easily heated. Another well-known fact is that ferro-magnetic metals can be heated more, which indicates that magnetism is tightly connected to the heating mechanism. Walkievics (1988), while testing the heating of various metallic powders, reported an interesting experimental result which demonstrated that there are differences in their heating rates. Some reports related to heating of metals (cermets, composites) were presented in the 1991 and 1992 MRS symposia, (Lorenson et al., 1991; Bescher et al., 1992). Mingos and his co-workers researched the synthesis of a metal sulfide by microwave heating of metals (Whittaker and Mingos, 1995). Roy and collaborators (1999) reported the successful microwave sintering of metals. Later on, they investigated the heating of metals in the separated Electric (E-) and magnetic (H-) microwave fields (Cheng et al., 2002; Roy et al., 2002). Research on microwave metal heating was carried on also in Europe (Rodiger et al., 1998; Leonelli et al., 2008). This research motivated the MW investigators to a more intense pursue of the study of metal heating.

A special symposium on metal heating was held in the annual meeting of the Japan Institute of Metals in 2005. Yoshikawa published a major review article (Yoshikawa, 2009) in which the recent results were presented and the application areas were classified.

The separated electric and magnetic microwave heating is directly related with the basic principles of the microwave heating mechanisms and of the microwave interaction with materials.

The various types of industrial wastes (mill scale, slag, dust, sludge etc.) contain useful elements such as Fe, Zn, etc., and consequently many researchers have suggested various methods for recycling the valuable metals. The most recent technology under investigation is microwave processing.

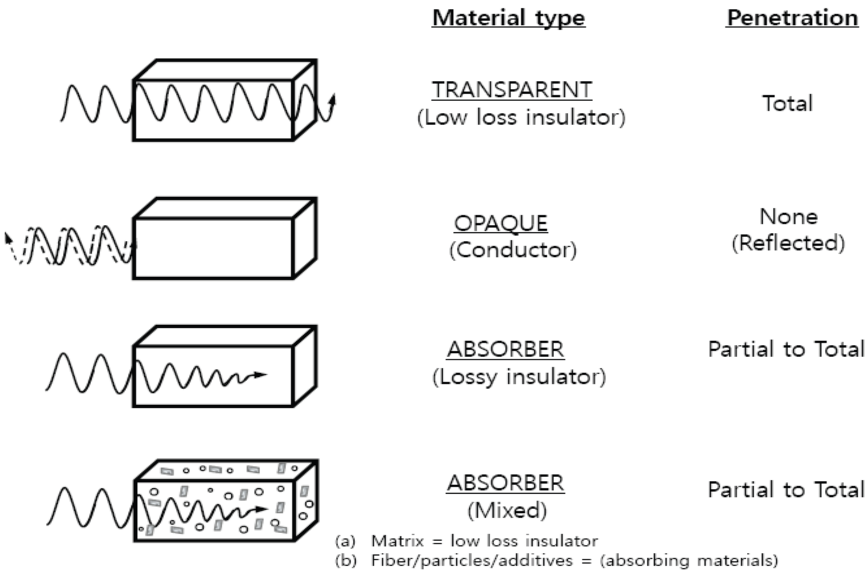

Fig. 2. *Material behavior in a microwave field*

Microwaves are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz and with wavelengths of microwaves ranging from 1 mm to 1 m, which is much larger than the molecular (nm) or crystalline (μm) grain size. Therefore, microwaves can provide energy to the valence electrons, leading to electron fluctuations. Microwaves can be absorbed, transmitted, or reflected, depending on the material type (figure 2). When microwaves are absorbed in a material, the electron fluctuation is finally transferred to the lattice ions and they create vibrations in the atomic lattice, resulting in heating energy. The heating rate varies with the electromagnetic properties of the material (complex permittivity and permeability), and the average power which can be absorbed by a material is the sum of the electric and the magnetic losses.

When microwaves are concentrated in a certain location on the material, the local temperature becomes higher than in the neighboring areas. As the local temperature surpasses a critical value, the heating rate becomes much higher, leading to the acceleration of the heating rate of the surrounding areas. This sudden thermal behavior can be very useful to significantly accelerate high temperature reactions and to diminish energy consumptions. Standish and Huang successfully recovered the metallic component from magnetite and hematite using microwave heating and reported that the microwave heating was five times faster than the conventional heating (Standish and Huang, 1991).

The microwave furnace is composed of three major elements: the microwave source, the transmission lines and the applicator (Das et al., 2009). The process is performed in a metallic applicator, which can be a traveling wave applicator, a single mode applicator or a multimode applicator, depending on the material to be processed. The single mode applicator and the traveling wave applicator are designed for processing materials with a simple geometry. The multimode applicator is used to produce large components with complex features and thus it is used for industrial applications. The material contained in the applicator absorbs or reflects the electromagnetic radiation generated by the source and delivered by the transmission lines (Thostenson and Chou 1999).

EXPERIMENTAL RESEARCH FOR MELTING E-WASTES IN A MICROWAVE FIELD

Hereafter are presented the results of experiments carried on for melting electrical and electronic equipment wastes (WEEE). The design of the experimental installation for the recovery of non-ferrous metals by using microwave energy for melting metallic wastes is given in figure 3.

The installations mainly consist of the steel casing of the furnace (1), on which three microwave generators are mounted on the exterior. The microwave susceptor graphite crucible (4), in which the metallic waste is contained, is placed inside the furnace. For eliminating the heat losses through the chamber walls, between the exterior wall of the crucible and the furnace chamber a thermal isolation layer (2) is placed, manufactured from super aluminous ceramic fiber and resisting temperatures of up to 1600^0C. The heating of the material is carried on using three microwave generators (6) of 800 W each, mounted on the furnace walls. In order to diminish the risk of metals oxidation during melting, a melting flux is added (a mix of NaCl + KCl in a 1:1 ratio) in quantities representing 5-10 wt.% of the total waste quantity, and the furnace is designed with a system for obtaining an inert nitrogen atmosphere, at a pressure of approximately 0.5 bar. Inside the crucible, the temperature is measured using a wire Pt/Pt-Rh thermocouple (8).

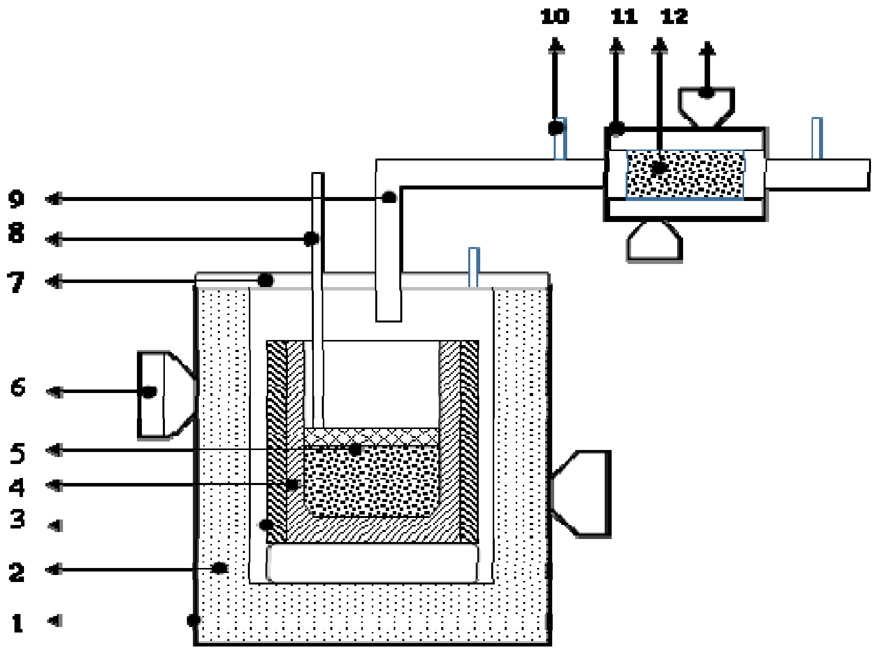

Fig. 3. *Design of the experimental installation for the recovery of nonferrous metals from metallic wastes by melting in a microwave field: 1. Furnace body (steel); 2. Thermo-insulating material; 3. Microwave susceptor material (SiC); 4. Graphite crucible; 5. Crushed PCBs+Fluxes charge ; 6. Microwave generators; 7. Furnace cover (steel); 8. Thermocouple (Pt/Pt-Rh); 9. Gas exhaust tube (steel) ; 10. Gas sampling tube; 11. Microwave field gas treating filter; 12. Microwave susceptor material (SiC pellets); 13. Microwave generators.*

The PCB wastes used in the experiments require a melting temperature of approximately 1000 ÷1200^0C. The flowchart of the melting process in a microwave field is given in figure 4.

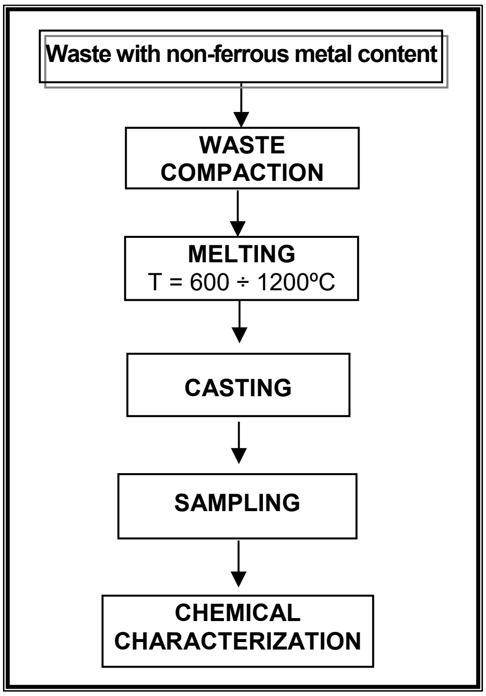

Fig. 4. *Flowchart of the melting process for wastes with non-ferrous metals content*

WEEE which result from the dismantling of electric and electronic equipment come in the form of powders with particle sizes of approximately 0.5-2 cm (figure 5). The powder contains approx. 50% organic fraction and ceramic components.

Fig. 5. *Grinded electric and electronic equipment wastes*

The wastes are mixed with the flux (NaCl + KCl in a 1:1 ratio), which represents 5% of the total waste quantity (calculated at an approximately 50% non-ferrous metal content in the waste). The mixture is introduced in the graphite crucible and is heated in the furnace using microwave energy, in a first step from 300 to 500^{0}C, when the pyrolysis of the organic materials present in the grinded printed circuit boards takes place. Subsequently, the temperature is risen to approx.1100^{0}C for melting the non-ferrous metals which have higher melting points, respectively: Cu (preponderant), Au, Ag.

The resulting multi-component alloy is casted as ingots (figure 6). The analysis of the chemical composition is presented in table 2. The metal recovery efficiencies were of approx. 44 ÷ 46%, the organic and ceramic fractions representing almost 50% of the initial wastes.

Fig. 6. *Multi-component alloy ingots resulting from the melting of WEEE in a microwave field*

Table 2. *Chemical analysis of the multi-component alloy resulting from the WEEE melting, %*

Cu	Al	Sn	Zn	Pb	Fe	Ni	Sb	Si	Mg	Mn	Au	Ag	Pd
rest	0.056	31.5	7.8	6.2	0.26	0.78	0.17	<0.1	<0.005	<0.002	0.016	0.075	0.0082

The experimental conditions of the gas treatment process are given in the table 3 and the results are presented in table 4. The emissions were measured at the exhaust outlet located behind the thermal filter that is positioned at the top of the melting furnace. The sampling was performed using the non-extractive method that did not require sample absorption and was limited to the gas flow existing in the pipe. The sampling plane was located in a section of the waste gas pipeline where homogeneous flow conditions and concentrations are expected, away from any fluctuation which could result in a change in effluent direction (a pipe section with a right line length of at least 5 hydraulic diameters upstream and 2 hydraulic diameters downstream of the sampling plane).

Table 3. *Experimental conditions for the treatment of gaseous emissions in microwave field*

Temperature [°C]	Gases flow [m^3/min]	Material filter	No. of magnetrons
1300 ÷1400	0.1 ÷ 0.2	SiC (pellets)	3 @ 850 W

Table 4. *Chemical composition of the effluent gases before and after the microwave thermal treatment*

Components	Concentration, [mg/m^3]		
	Out furnace		Out filter
	$T_{furnace}$ 300ºC	$T_{furnace}$ 500-800ºC	T_{filter} 1300-1400ºC
Ethyl chloride	6.42	1.37	-
Methyl chloride	1.95	0.76	0.08
Ethylic alcohol	1.25	0.42	0.028
Butanol	6.06	0.92	0.05
Benzene	5.43	14.70	0.035
Ethylbenzene	-	1.31	0.072
Styrene	-	0.37	0.098
Toluene	1.07	2.88	0.06
m/pXilen	-	1.56	0.004
Acetone	105.70	1.80	-
Bromomethane	82.57	-	-
Trimethylbenzene	1.35	5.30	0.015

A TESTO 435 analyzer was used for the determination of the exhaust gas physical parameters (rate, temperature, pressure).

It can be observed that the treatment of the resulting exhaust gases in a microwave environment at a temperature of 1300 ÷ 1400°C lead to a reduction of up to 98% of the toxic compounds by thermal neutralization.

CONCLUSIONS

Compared to the classical pyro metallurgical technologies for the processing of non-ferrous metal wastes, microwave melting represents a modern, ecological and efficient alternative, with high applicability. The process presents as main advantages: low melting time with energy savings of approximately 35% in comparison to conventional methods; an improved process control; lack of direct contact with the melting materials; Environmental friendly process, due to the possibility of treating the toxic gases resulting from melting wastes in a special microwave installation.

A complete separation of the organic components and metallic fraction was achieved by melting PCBs in a microwave furnace. The efficiency of metal recovery was higher than 96%.

The treatment of the resulting exhaust gases in a microwave environment at a temperature of 1300 ÷ 1400°C lead to a reduction of up to 98% of the toxic compounds by thermal neutralization.

The preliminary experiments demonstrated that the melting of crushed PCBs in a microwave field furnace is an efficient and environmentally friendly route for the recovery of metals, with low energy and time consumptions.

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