WHITE METAL BEARING WASTE MELTING AND RESULTED NOXIOUS GASES PROCESSING IN MICROWAVE FIELD

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Abstract: Microwave heating and melting of mterials receive considerable attention due to their major advantages such as: high heating rates, reduced processing time, low power consumption, better product performance as well as less environmental hazards. The recent aplications of microwave in the field of metallic materials are sintering, brazing/joining and melting. Thewhite metal waste (Sn-based and Pb-based alloys) melting in microwave (MW) furnace as well as the resulted noxious gases treatment in a microwave heated thermal filter has been preliminary investigated.
Key words: white metal waste, melting, microwave field, noxious gases, microwave thermal filter

1. INTRODUCTION

White metals are any of several tin-based or lead-based low melting point alloys used for things like bearings, fusible plugs, metal type, miniature figures, etc. A white metal may include as alloying elements: antimony, cadmium, copper, bismuth, zinc, magnesium, calcium, etc. (Matucha, 1996; Habashi, 2008). Significant quantities of white metal wastes are generated by the bearing industry (OCDE, 1995).
Reverberatory and electric furnace melting is the main procedures used for the white metals obtaining and waste recovery (Ienciu, 1985). This raises major issues because of the generated volatile elements emissions as well as low recovery efficiency due to the metal oxidation (Malcharcziková, 2016).
The recycling of these alloys scrap could reduce the environmental impact as they contain some toxic elements (Cd, Pb, Zn, etc). Also, there is an economic impact due to the high price of the constituent elements of the alloys (Rademaekers, 2011).
The actual prices of principal metal constituent of the bearing alloys are presented in Table 1.
Microwaves (MW) are electromagnetic radiations with frequency ranging 300MHz and 300GHz and wavelengths in the range of 1mm - 1m, much larger than the size of the molecules (nm) or the metallic crystalline grains (μm). As a result, part of the energy of the electromagnetic field is transformed into thermal vibration energy and transferred to the molecules of the melted material (Das et. al 2009).

Table 1. Metal price [9]

	Sn	Pb	Sb	Zn	Cu
USD/ton	17800	2050	6000	2450	6080

This generates a heating effect of the dielectric material which is caused partly by the polarization of the charged particles from the material by the high frequency electric field (hysteresis losses), and partly by the Joule effect due to the conduction of the free loads under the action of the electric field. By controlling the form of microwave heating along with appropriate thermal insulation, very high temperature can be achived with relatively low microwave power (Gupta et.al, 2007).
Microwave (MW) melting of metals is a novel technology which presents major advantages compared to the classical pyrometallurgical processes, such as simultaneous evolution of the heating gradient in the entire volume of material, a much higher heating rates that shorten the melting time by (70-85)% and allow energy savings and higher processing capacities and a superior quality of the obtained materials by reducing the melt impurification through oxidation (Agrawal, 2006,Chandrasekaran et.al., 2011).
The use of microwaves MW in materials processing provides an important instrument to melt a wide range of materials under different conditions, as metallic wastes with a wide range of shapes, chemical compositions and structures can be processed in the same installation (Appleton et.al., 2005).
Low melting point metals (Sn, Pb, Bi, Al) also were subjected to MW furnace melting and processing in order to determine their behaviour under MW irradiation (Sun et.al, 2005).

Microwave heated ceramic granular filter also offers the possibility of treating the noxious gases emissions during the waste melting, particularly organic volatile compounds (Heidenreich, 2013).
In this paper, the melting of white metal waste in microwave (MW) furnace as well as the treatment of gas emissions in a microwave thermal filter has been preliminary investigated.

2. EXPERIMENTAL

The waste was purchased from specialised non-ferrous metal recycling enterprises and consists in spoiled castings, pouring gates, risers, and machining, used bearings. Some pieces of metal waste are contaminated with oil and vaselineoil.The waste used in the experimental works is shown in Figure 1.

Fig. 1.White metal waste

The chemical analyses of the representative white metal waste samples, performed by ICP-OES (according to ASTM E 1479-16 standard) are presented in Table 2 and Table 3 respectively.

Table 2. Chemical composition of tin-based alloys waste

Element [wt.%]					
Sb	**Cu**	**Pb**	**Zn**	**Others**	**Sn**
8.9	6.31	0.5	< 0.1	< 0.5	balance
9.7	5.78	0.2	< 0.1	< 0.5	balance
6.85	6.92	0.7	< 0.1	< 0.5	balance

Others: Al, Cd, Mg, S, Si:< 0.1% each

Table 3. Chemical composition of lead-based alloys waste

Element [wt.%]					
Sb	**Sn**	**Cu**	**Zn**	**Others**	**Pb**
9.7	9.2	0.8	0.18	< 0.5	balance
10.5	8.7	1.5	0.1	< 0.5	balance
12.2	9.8	1.2	0.15	< 0.5	balance

Others: Al,Cd, Fe, Mg, Si, S: < 0.1% each

Experimental set-up.
The draft of the laboratory experimental MW equipment for melting nonferrous metals waste is shownin Figure 2.
The melting equipment consists of a cylindrical enclosure made of steel (1), in which are five rectangular windows for mounting the microwave generators (6). The axes of the windows are positioned in different horizontal planes, the angle between the axes is 72°, thus radiating different areas of the susceptor material (3). In order to reduce the heat loss, the interior of the enclosure is covered with a thermal insulation layer (2) made of super-alumina ceramic fibres with resistance to temperatures up to 1600°C. Coaxial, there is placed the melting crucible (4), made of graphite-clay mixture, approx. 1 litter capacity, clothed in a microwave susceptible material (3) made of silicon carbide. The batch heating is performed by five microwave generators (magnetrons) of 2.45GHz and 850W power (6). The temperature is measured using a ceramic sheath K-type thermocouple (8).

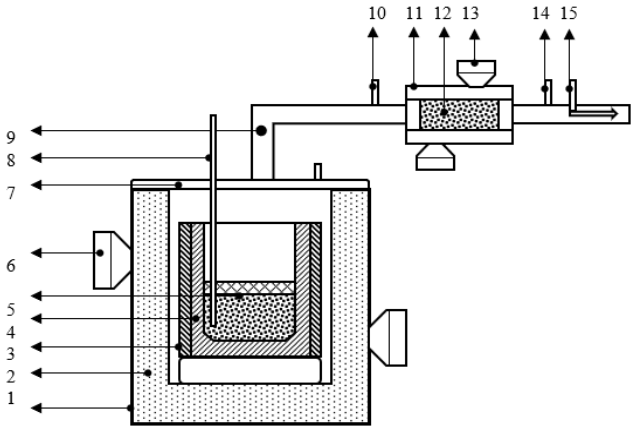

Fig. 2. Microwave melting furnace and gases thermal filter: *1. Furnace body (steel); 2. Thermal insulating material; 3.MW susceptor material (SiC); 4.Melting graphite crucible; 5.Charge (Al cable waste+cover flux); 6.Furnace MW magnetrons; 7.Furnace cover (steel); 8.Thermocouple (K-type); 9.Flexible exhaust tube (steel); 10. Gas sampling socket pipe; 11.Burning gases thermal filter treating; 12.MW susceptor material (SiC balls); 13.Filter MW magnetrons; 14.Dust sampling socket pipe; 15.Venturi tube*

The laboratory MW experimental non-ferrous waste melting installation is presented in Figure 3.

Fig. 3. Laboratory microwaveexperimental waste melting installation

Generated noxious gases and dust are captured through the exhaust pipe (9), fixed in the furnace cover (7), and which is connected with the gas treatment thermal filter (11). The filter consists of a steel cylinder in which windows are cut out for the

installation of three magnetrons of 2.45GHz and 850W power (13). A microwave transparent quartz cylinder is placed inside the steel cylinder and contains a microwave susceptible material SiC (12) in the form of (8-10)mm diameter balls. The temperature inside the thermal filter is measured with a K-type thermocouple. Gas and dust sampling are carried out through nozzles (10, 14) attached to the exhaust tube (9) just before and after the filter.

Experimental procedure

The metallic waste was cut into small pieces (approx. 2-3 cm length) which were feeded in the MW furnace crucible. Dried active carbon powder (Sigma Aldrich, 200-325 mesh) was used as melting protective flux. After feeding the charge, the melting process was started by electric supply of the MW magnetrons of furnace and thermal filter respectively. To force the evolved gases to pass through the thermal filter, a constant compressed air flowwasblowed into Venturi tube.

After the melting of the waste charge, in order to homogenise the composition, the melt was lightly stirred with a graphite bar. The slag was collected with a skimmer and the melt was poured in a cast-iron mould.

In the first series of experiments, the influence of flux/waste ratio was investigated. The melting temperature was set up to 400°C for Sn-based waste and 500°C for Pb-based waste respectively.

Based on the analysis of the first series ofexperiments, the parameters to the second series ofexperiments were defined.In this second series, the melting temperature was investigated at a constant flux/waste ratio (F/W=0.1).

The experimental parameters for waste MW meltingarepresented in Table 4

Table 4. Waste MW melting process parameters

Parameters	Values
Melting time [min]	20 - 30
White metal waste quantity [g]	500±1
Cover flux (active carbon) [g]	10 – 50 ±1g
Flux/waste (F/W) ratio	0.02 -0.1
Waste melting temperature [°C]	Sn-base: 500 - 550 Pb-base: 450 - 500
MW thermal filter temperature [°C]	700 - 900
Thermal filter blast air debit [l/min]	5 - 8

During the melting of the waste, samplings of evolved noxious gasesfor the content determination of metals as well as VOCswere extracted from the exhaust tube, just before and after the MW thermal filter.

Volatile Organic Compounds (VOCs) were captured on CSC Anasorb cartridges according to standard SR EN 13649:2002. The VOCs were desorbed on dichloromethane and analysed by a gas chromatograph mass spectrometer GC-MS QP 2010 Plus apparatus.

Metallic particles/dust was captured on polytetrafluoroethylene (PTFE) filters 2.0µm pore size. An X-ray spectral analyser Niton XL3T apparatus was used for the determination of the metal content in thesample.

3. RESULTS AND DISCUSSIONS

The results of the first series of white metal waste MW melting experiments are presented in Table 5.

Table 5.The experimental results of the waste MW melting

Charge no.	*IN*		*OUT*		η [%]
	Metal waste [g]	Flux [g]	Metal [g]	Slag [g]	
1.	Sn-based waste - 500±1	10	415.5	91.4	83
2.		25	435.6	87.6	87
3.		50	476.2	72.8	95
4.	Pb-based waste - 500±1	10	361.3	146.7	72
5.		25	421.2	98.3	84
6.		50	449.7	97.6	90

Fig. 4. Metal ingots recovered from white metals waste

The chemical composition of the metal revovery ingots are presented in Table 6 and Table 7 respectively.

Table 6. Chemical composition of the recovered Sn-based white metals

Charge no.	Sb	Cu	Zn	Pb	Others	Sn
1.	8.3	6.4	<0.01	0.4	<0.5	balance
2.	8.7	6.1	<0.01	0.7	<0.5	balance
3.	9.1	6.8	<0.01	1.6	<0.5	balance

Others: Al, As, Bi, Ca, Cd, Fe, Mg, etc.

Table 7. Chemical composition of the recovered Pb-based white metals

Charge no.	Sb	Cu	Zn	Sn	Others	Pb
4.	8.9	1.1	<0.1	7.8	<0.5	balance
5.	9.7	1.3	0.2	9.1	<0.5	balance
6.	9.2	1.7	0.2	9.5	<0.5	balance

Others: Al, As, Bi, Ca, Cd, Fe, Mg, etc.

In Figure 5 are presented the metal recovery efficiency vs. flux/waste ratio diagram.

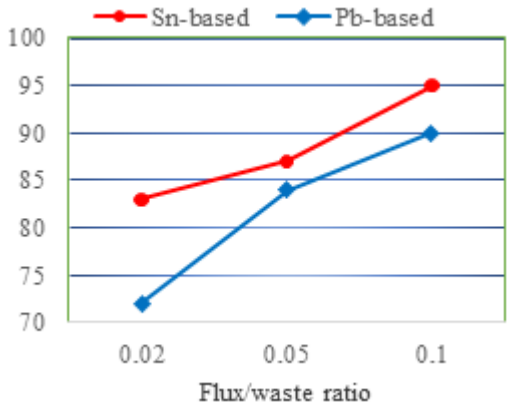

Fig. 5. MW metal recovery efficiency vs. flux/waste ratio

As could be seen in diagram, the recovery efficiency increases with increasing of the flux quantity (active carbon) used for melting.Using a thick layer of protective flux results in a better protection of the melt against oxidation during the meltingprocess.Also, a good explanation of the increasing efficiency could be the more favourable conditions for oxide reduction (SnO, PbO) in the presence of an excess of melting flux (active carbon, as well as CO and CO_2 formed during the heating).

The results of the first series of white metal waste MW melting experiments are presented in Table 7.

Table 7. The experimental results of the waste MW melting

Ch. no.	Temp. [°C] ± 5°	*IN*		*OUT*		η [%]
		Metal waste [g]	Flux [g]	Metal [g]	Slag [g]	
7.	425	Sn-based 500±1	50	474.3	68.7	95
8.	450			478.9	71.5	96
9.	525	Pb-based 500±1	50	448.7	88.3	90
10.	550			459.2	91.8	92

In Figure 6 and Figure 7 are presented the metal recovery efficiency vs. melting temperature for Sn-based waste alloys and Pb-based waste alloys respectively.

Increases in melting temperatures leads to small increases in efficiency recovery values: 1% for Sn-based waste and up to 2% for Pb-based waste respectively.

This could be due to the increased fluidity of the metallic bath with result on better separation metal-slag.

Also, increased melting temperature could result in accelerating the metal oxidation reaction as well as evaporation of the volatile elements (Pb, Zn, Cd) which results in decreasing recovery efficiency.

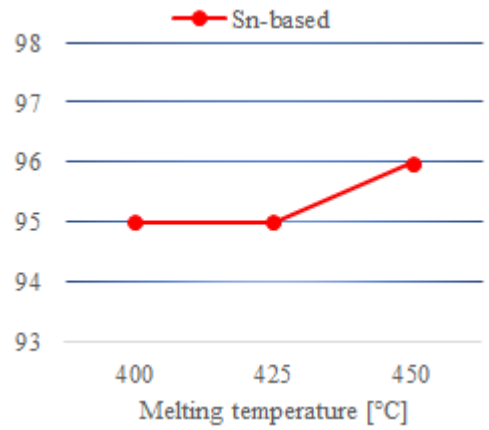

Fig. 6. Sn-based metal recovery efficiency vs. melting temperature (F/W ratio = 0.05)

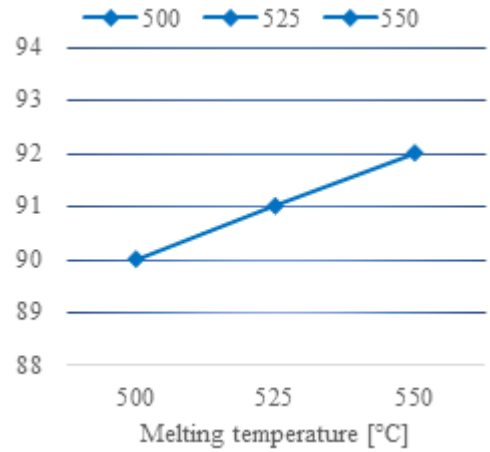

Fig. 7. Pb-based metal recovery efficiency vs. melting temperature (F/W ratio = 0.05)

The chemical composition of the evolved noxious gases duringthe MW melting *(OUT furnace)*and after the treatment of the gases in MW heating thermal filter*(OUTTF)*are presented in the Table8 for Sn-based waste and Table9 for Pb-based waste respectively.

Table 8. The chemical composition of the evolved gasesduring the MW melting of Sn-based waste [mg/Nm^3]

Element	OUT furnace	OUT TF Temperature of MW thermal filter [°C]			Legal limits*
		700	800	900	
Sn	8.31	2.38	2.23	0.43	5
Pb	0.55	0.2	0.18	0.12	5
Sb	0.05	0.11	0.01	0.01	5
Cu	2.63	0.18	0.14	0.05	5
Zn	1.71	0.65	0.55	0.41	5
Cd	1.62	1.23	0.24	0.01	0.2
VOC_{Total}	53.68	15.76	4.19	0.64	-
Acetone	12.02	0.61	0.12	0.01	5
Benzene	10.17	5.82	1.22	0.9	5
Etilbenzene	3.15	2.3	0.23	0.1	5
Butanone	3.49	1.32	0.2	0.1	5
Toluen	2.23	0.84	0.1	0.1	5
Xylene	8.37	5.08	0.55	0.2	5

Table 9. The chemical composition of the evolved gases during the MW melting of Pb-based waste [mg/Nm^3]

Element	OUT furnace	OUT TF Temperature of MW thermal filter [°C]			Legal limits*
		700	800	900	
Pb	8.59	3.61	2.63	0.24	5
Sn	0.44	0.43	0.01	0.01	5
Sb	0.1	0.01	0.01	0.01	5
Cu	2.88	0.25	0.19	0.3	5
Zn	6.61	0.77	0.47	0.4	5
Cd	2.97	1.62	0.1	0.09	0.2
VOC_{Total}	48.64	6.38	1.07	0.85	-
Acetone	10.62	0.56	0.1	0.1	5
Benzene	8.96	3.74	1.08	0.62	5
Etilbenzene	2.18	1.4	0.22	0.1	5
Butanone	2.06	1.05	0.18	0.1	5
Toluen	1.87	0.53	0.1	0.1	5
Xylene	7.95	4.2	0.13	0.1	5

*) Legal limits according to the document: *Order no. 462/1993*

The content of metals and VOCs respectively in the evolved gases during the MW melting *(OUT furnace)* and after the treatment of the gases in MW heating thermal filter *(OUT TF)*, heated at different temperaturesare presented in the Figure 8 and Figure 10 for Sn-based waste and Figure 9 and Figure 11 for Pb-based waste respectively.

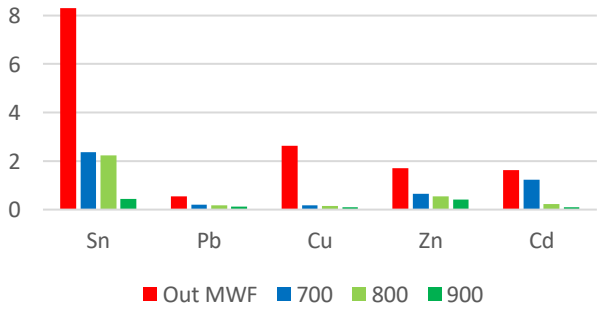

Fig. 8. The metals content in the gases for Sn-based waste MW melting and after the treatment in MW thermal filter

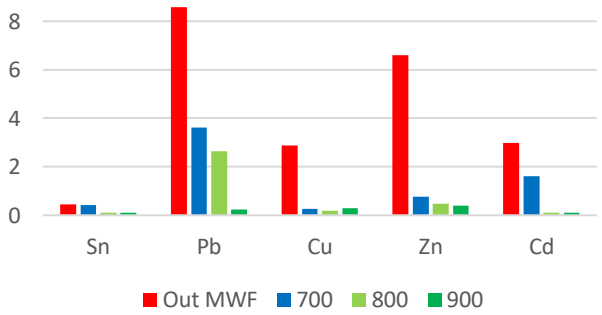

Fig. 9. The metals content in the gases for Sn-based waste MW melting and after the treatment in MW thermal filter

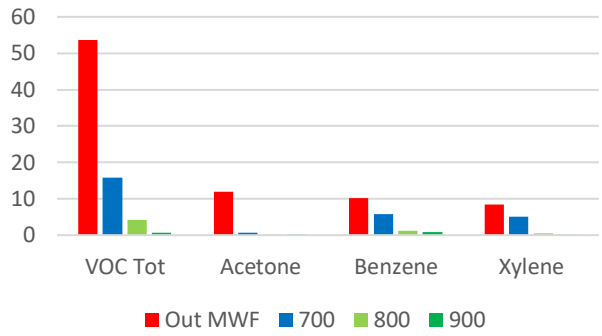

Fig. 10. The VOCs content in the gases for Sn-based waste MW melting and after the treatment in MW thermal filter

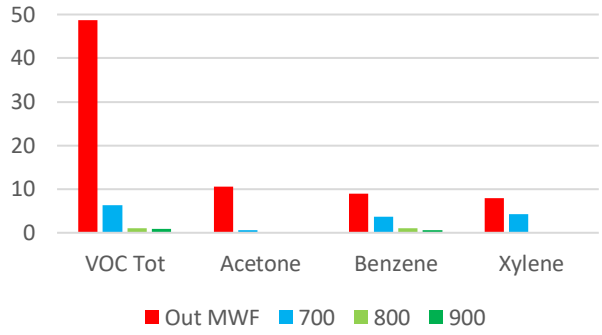

Fig. 11. The VOCs content in the gases for Pb-based waste MW melting and after the treatment in MW thermal filter

From the chemical analysis of the sampling data presented in the Table8 and Table9, during the melting of the white metal waste, noxious gases are generated. There is a higher content of metal base Sn and Pb respectively, as well as of the minor alloying element Zn and Cd;themetalscontent is higher than the legal limits (5mg/Nm^3 for Sn, Pb, Zn, etc. and 0.2mg/Nm^3 for Cd respectively).

Also, the VOC content (product of the oil and vaseline oil impuritiesburning) are high, exceeding for some components (acetone, benzene, xylene) by 2-3 times the legal limits (5mg/Nm^3).

Others VOCs determined in the evolved gases, but at values << 1 mg/Nm^3 are: Styrene, Propyl-benzene, Butyl-benzene, Ethyl alcohol, Butanone, Hexanone, Dichlorbenzene, etc.

By passing the noxious gases through the MW granular ceramic thermal filter heated at 700°C the metal contentsdrop the legal limit except for Cd. Heating the filter up to 900°C reduces the Cd content below the legal value (0.2mg/Nm^3).

As regards VOCs, at a temperature of the thermal filter of 700°C only small exceeding for benzene and xylene are recorded (in the case of Sn-based waste melting). Increasing the temperature of the thermal filter up to 900°C, VOCs' total content is reduced below 1mg/Nm^3.

4. CONCLUSIONS

The results of the preliminary experiments confirm the feasibility of the MW melting of the white metal waste (Sn-based and Pb-waste) as well as the evolved noxious gases treating in a MW ceramic granular heating filter.

With increasing the flux/waste ratio (0.02-0.1), the recovery efficiency increased up to 90% for Pb-based and 95% for Sn-based alloys respectively.

Increasing the melting temperature, only a small increase in the metal recovery efficiency was recorded: 1% for Sn-based waste and 2% for Pb-based waste respectively.

During the melting of the waste, noxious gases such as volatile metals, metals and oxide dust as well as VOCs (as result of oil and vaseline burning) are generated.

The temperature of the MW thermal filter has a major influence in the retention and neutralization of the noxious compounds evolved during the melting (in special on VOCs) up to level below the legal limits.

The mechanisms of retention of metal dust and VOCs neutralization in the MW ceramic granular thermal filter have to be elucidated by further researches.

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