PRODUCTION OF METALLIC NANOPARTICLES, FROM INDUSTRIAL RESIDUES, BY THE USE OF DIFFERENT TYPES OF REDUCTION GASES

P. PEIXOTO[1*], D. SOARES[1] and F. CASTRO[2*]

[1] CT2M - Centre for Mechanical and Materials Technologies, Mechanical Engineering Department of Minho University, Guimarães, Portugal.

[2] CVR – Centro para a Valorização de Resíduos (Center for Waste Valorization), Guimarães, Portugal.

*Corresponding author at: fcastro@dem.uminho.pt (F. Castro), Tel.: +351 253510025; fax: +351 253510029.

Keywords: Metals recovery, sludge treatment, metal nano-particles

Abstract

The need to enhance and reuse existing materials on secondary sources of metals has had quite an impact in recent times. Several processes and technologies had being studied for recovery of raw materials from industrial waste generated. This study focuses on the possibility of waste reducing, from the galvanic floor covering industry, with the aim of obtaining micro or nano-particles of nickel or a nickel based alloy.

Sludges from one galvanic treatment plant were used as base material in two conditions: as produced and after a hydrometallurgical treatment for metal concentration. Several reducing agents were used in this study: a synthesis gas from a polymer pyrolysis and solid polymer agents (PVC, HDPE and PP residues). Obtained products were characterised in terms of metallic particles production during the reduction treatment and by SEM/EDS analysis on the final products.

A simultaneous differential thermal and thermogravimetric equipment (DSC/TGA) was used for the study of the reduction process with a reduction gas obtained from the pyrolysis of chlorine free PVC derived char. The obtained results show that it is possible to obtain small metallic particles, in the range of 60 to 240 nm, at 800 ºC.

Reduction tests, by the use of a solid residue, were made in a laboratorial furnace with two independent heating zones. Best results were obtained with de-chlorinated PVC as a reduction agent with the production of metallic particles, in the range of 150 to 600 nm, at 800 ºC. For all the tested conditions the metallic particles were constituted by Ni and Cu with variable chemical composition.

1- INTRODUCTION

Galvanic sludge's are an example of industrial residues with high recycling potential. Usually they have high contents of metallic elements as Ni, Cu, etc. These products are classified as toxic materials because of the high concentration of some leachable metallic elements (Cr, Ni, Pb, etc) with high environmental impact [1, 2]. Landfill disposal is not possible and so large volumes of material must be treated to reduce their toxicity. The residue chemical composition might changes for different production plants introducing some difficulties in the establishment of the reduction process parameters [2]. The presence of elements with economical value is also an opportunity for metallic recovery treatments development. Particles of Ni, with nanometric size, present several interesting applications in the fields of permanent magnets, solar energy absorption, fuel cell electrodes, etc [3, 4].

Another residue type with recycling interest is polymer materials. The main fraction of polymer residues is disposed on landfills, with high environmental impact caused by phthalate and heavy metals leach out. On thermal treatments polymers releases significant amount of gases with reducing properties (carbon based compounds) [5, 6, 7, 8, 9].

In this work two types of reducing gases were tested for metal particles recovery, with nanometric scale size, from a galvanic sludge. Firstly, was used a synthesis gas obtained from a PVC based residue treatment. A second series of tests were made using reducing gases obtained from thermal decomposition of polymers different types.

2- MATERIALS AND METHODS

This work employed an industrial sludge from a galvanic plant producing chrome platting of plastic goods. A hydrometallurgical sludge treatment allows the obtainment of a Ni or Ni hydroxide rich product. This galvanic sludge treatment was made at Centro para a Valorização de Resíduos (CVR). Both types of products, with and without initial treatment, were used in this work. Sludge composition is presented in Table 1.

Table 1 – Industrial sludge composition, before and after the initial treatment.

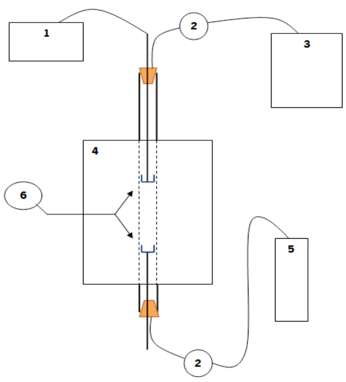
Compound	Sludge composition (wt%)	
	initial	After treatment
Al_2O_3	0,254	0,210
CaO	18,2	0,351
Cl	0,517	0,621
Cr_2O_3	22,2	0,252
CuO	12,2	1,41
Fe_2O_3	0,184	1,00
MgO	0,391	0,450
Na_2O	1,53	2,83
NiO	17,9	83,7
P_2O_5	18,4	0,425
SO_3	7,01	8,13

Reduction gases, obtained from the thermal decomposition of three types of polymers (PEAD, PP and PVC), were used in this work. A synthesis gas, from a polymer thermal decomposition was, also, used. For the PVC polymer an initial pyrolysis treatment was made (at 350 ºC) in order to eliminate the chloride present.

The thermal decomposition of the polymers was studied by DSC/TGA to define the temperatures for the reduction tests.

DSC/TGA equipment was, also, used to study the reduction reactions of the metallic elements in the residues. These tests were conducted in two steps: a first one, to heat to the reaction temperature (800 ºC) in an inert atmosphere (argon flow) and a second one, after temperature stabilization, when the valve for the entrance of synthesis gas is open (argon flow is stopped) and the reduction reactions take place. The synthesis gas was produced from an energetic valorization process (at 800 ºC) of a PVC de-chlorinated fraction from an industrial PVC based residue [10]. The gas is constituted by 40 % H_2, 17% CO, 5% CO_2, 11% CH_4, 11,8% H_2O (in vol. %).

A second series of tests were made in a closed vertical resistance furnace with two independent heating zones (Figure 1). Polymer materials were placed at the bottom part, at 600 ºC, and the test sludge at the upper part, at 800 ºC. The test is divided in two parts: initially the upper zone, with the sludge sample, is heated up to the 800 ºC in an argon atmosphere; when the temperature is stabilized the lower heating resistance is turned on and temperature is raised up to 600ºC, at a rate of 10ºC/min. The temperatures are maintained for 30 min., in order to allow the thermal decomposition of the polymer powder placed on the bottom part. Produced reducing gases from the polymer flow through the sludge particles and leave the furnace on the upper part (gas bubbling in a water reservoir, out of the furnace, to avoid air entrance in the system).



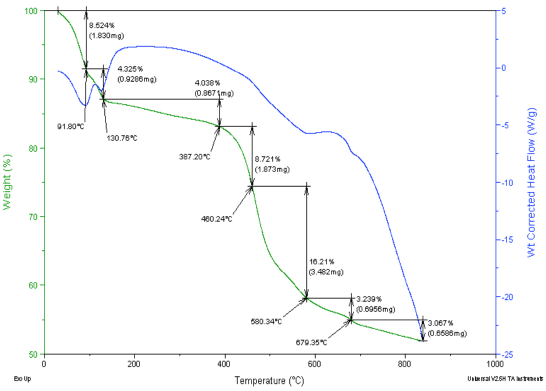
1 – thermocouple and temperature controller;
2 – gas valves;
3 - gas bubbling reservoir;
4 – two zones resistance furnace;
5 – gas inlet (argon);
6 – sample support reservoirs (top crucible: sludge residue; down crucible: polymer).

Figure 1 – Schematic drawing of the two zone furnace and experimental scheme used for the reduction tests with solid polymers.

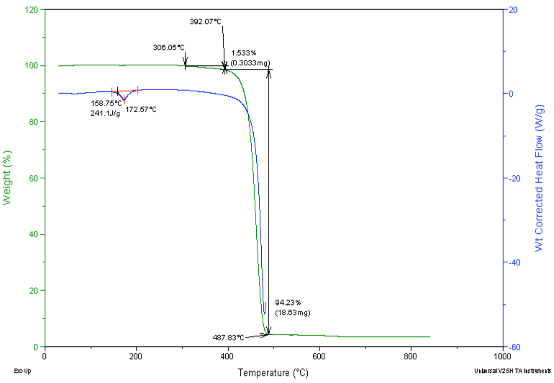
The obtained materials from the reduction tests were collected and analyzed by SEM in order to determine the presence, morphology, distribution and size of the produced metallic particles. Qualitative metallic particles chemical composition was obtained by EDS analysis.

3- RESULTS AND DISCUSSION

The first series of tests were made in the DSC/TGA system. The weight change and heat flow of polymer thermal decomposition are presented in Figure 2. A slow decomposition over a range of temperatures was obtained for the de-chlorinated PVC (between ~400 and ~800 ºC). In opposite, for the PEAD and PP, a very fast decomposition, at an almost constant temperature, was obtained. The reaction temperatures were of 390 and 380 ºC for, respectively, PEAD and PP polymers (Figure 2b). These behavior results in a very fast gas release for PEAD and PP and a more continuous gas flow for PVC.



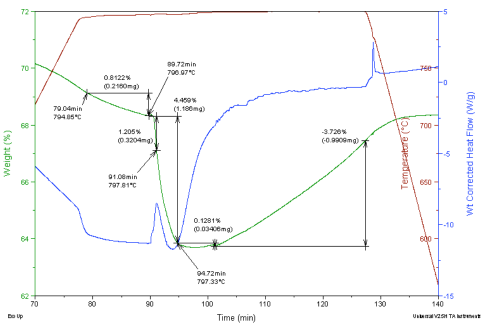
a)



b)

Figure 2 – DSC/TGA results for the thermal decomposition of the de-chlorinated PVC a) and PEAD b).

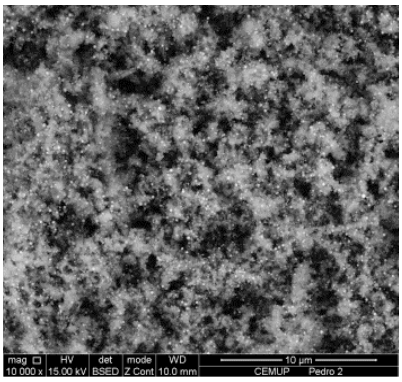
The reduction of the sludge powder with a synthesis gas was initially tested in the DSC/TGA equipment. The weight change and heat flow during the thermal cycle of the galvanic sludge with the constant flow of the synthesis gas is presented in Figure 3a. Less than 10% of weight loss is obtained during the first 80 min. (initial stage of heating in an inert atmosphere). When the synthesis gas valve is open (90 min.) there is a rapid exothermic reaction with a correspondent sample weight loss of ~85%. This weight variation results of the release of carbon based compounds from the sludge. From those reactions several metallic particles were produced. Figure 3c) and 3d) presents the metallic particles distribution, shape and size (dimensions from 60 to 200 nm). The particles chemical composition is, essentially, constituted by Ni and Cu (Figure 3b).



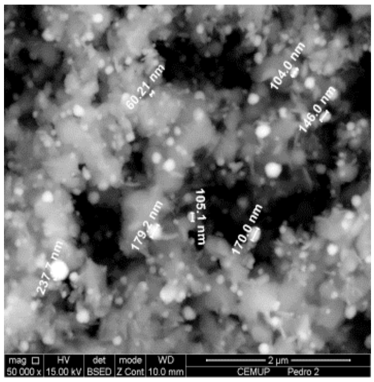
a)

	Chemical composition (wt%)	
	Initial sludge	Treated sludge
Ni	46	~98
Cu	54	-

b)



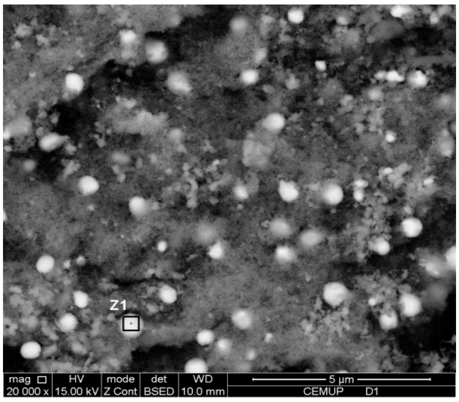
c)



d)

Figure 3 – DSC/TGA results for galvanic sludge reduction a), metallic particles chemical composition b) and metallic particles shape, size and distribution obtained with synthesis gas c) and metallic particles size d).

In the tests with solid polymers as reduction agents the best results were obtained with the de-chlorinated PVC. For de-chlorinated PVC tests small particles, of a Ni rich alloy, were produced with a good distribution all over the sample. Figure 4a shows the obtained metallic particles with homogeneous distribution, spherical shape and small size (dimensions from 150 to 600 nm). The particles chemical composition is, also, presented in Figure 4b. With PEAD and PP tests no significant metallic particles were detected in the final product. The different results should be a consequence of the very fast reduction agent gas production, with PEAD and PP polymers, resulting in a very short contact time between the gas and the sludge particles.



a)

	Chemical composition (wt%)	
	Initial sludge	Treated sludge
Ni	53	~98
Cu	47	-

b)

Figure 4 – Metal particles obtained with the reduction tests, of the sludge powder, with de-chlorinated PVC.

The metallic particles obtained on the DSC/TGA tests are smaller (60 to 240 nm) and with a slightly higher Ni content, for sludge samples reduction treatment, when compared with the obtained in the two zones furnace. The differences in the resulting metallic particles of both types of tests (DSC/TGA and two zones furnace) is attributed to different test conditions control. The temperature and, essentially, the gas flow control are more accurate in the DSC/TGA equipment.

4- CONCLUSIONS

Production of very small metallic particles from an industrial treatment galvanic sludge, on a DSC/TGA equipment, by the use of a synthesis reduction gas was made. The metallic particles have small size (60 – 240 nm) and spherical shape. The metallic particles are of a Ni-Cu alloy, with a Ni content of ~53 % (in wt.%). A previous treatment of the initial galvanic sludge, with increase on Ni content, allows the production of small and high purity metallic particles with ~98% Ni (wt%).

The adapted two zones furnace allows the decomposition of solid polymers for gas production and their use as reduction agent for the galvanic sludge. The polymer reactions must be controlled in order to have a controlled gas flow in terms of pressure (mass) and time. Too fast polymer decomposition reactions are not appropriated to promote the metal reduction reactions. Metallic nanometric particles (up to 600 nm) were produced with this equipment from a galvanic sludge.

The size and chemical composition of the final metallic particles are dependent of the process parameters. The control of reduction gas flow pressure and time of contact with the sludge is important for the final metallic particles characteristics (chemical composition and size).

REFERENCES

[1] - Rossini, G., Bernardes, A.M., Galvanic sludge metals recovery by pyrometallurgical and hydrometallurgical treatment. Journal of Hazardous Materials 131, 210–216, 2006.
[2] - Magalhães, J.M., Silva, J.E., Castro, F.P., Labrincha, J.A., Physical and chemical characterization of metal finishing industrial wastes. Journal of Environmental Management 75, 157–166, 2005.
[3] Ying, Z., Shengming, J., Guanzhou, Q., Min, Y., Preparation of ultrafine nickel powder by polyol method and its oxidation product. Materials Science and Engineering B 122, 222–225, 2005.
[4] Couto, G.G., Klein, J.J., Schreiner, W.H., Mosca, D.H., Oliveira, A.J.A., Zarbin, A.J.G., Nickel nanoparticles obtained by a modified polyol process: Synthesis, characterization, and magnetic properties. Journal of Colloid and Interface Science 311, 461–468, 2007.
[5] - Siddique, R.; Khatib, J.; Kaur, I.: "Use of recycled plastic in concrete: A review", Waste Management, 28, 1835-1852, 2007.
[6] - Al-Salem, S.; Lettieri, P.; Baeyens, J.: "Recycling and recovery routes of plastic solid waste (PSW): A review", Waste Management, 29, 2625-2643, 2009.
[7] - Takuma, K.; Uemichi, Y.; Ayame, A.: "Product distribution from catalytic degradation of polyethylene over H-gallosilicate", Applied Catalysis A: General, 192, 273-280 (1999).
[8] - Spinacé, M.; Paoli, M.: "A tecnologia da reciclagem de polímeros" Revisão, Química Nova, 28, 65-72, 2005.
[9] - William, E.A., Williams, P.T., Analysis of products derived from the fast pyrolysis of plastic waste. Journal of Analytical and Applied Pyrolysis, 40-41, 347-363, 1997.
[10] – A. Castro; D. Soares, C. Vilarinho, F. Castro, Kinetics of thermal de-chlorination of PVC under pyrolytic conditions, Waste Management, 32, 847–851, 2012.