MANUFACTURING TECHNOLOGY

JOURNAL FOR SCIENCE, RESEARCH AND PRODUCTION

The journal is indexed in SciVerse Scopus

February 2016, Vol. 16, No. 1
ISSN 1213–2489
Issued by J. E. Purkyne University in Usti nad Labem,
Faculty of Production Technology and Management.
Czech Republic. Europe.

Manufacturing
TECHNOLOGY

forced plastics using design experiments. In: *Journal of Materials Processing Technology*, Vol. 160, pp.160–167.

[5] EL-HOFY, M.H. ET AL. (2011). Factors affecting workpiece surface integrity in slotting of CFRP. In: *Procedia Engineering*, Vol. 19, pp. 94–99.

[6] GOTTFRIED W. E. (2009). *Polymer composite materials* (Polymerní kompozitní materiály). Scientia. Czech Republic.

[7] HINTZE WOLFGANG, W., HARTMANN, D., SCHÜTTE, C. (2011). Occurrence and propagation of delamination during the machining of carbon fibre reinforced plastics (CFRPs) - An experimental study. In: *Composites Science and Technology*, Vol. 71, No. 15, pp.1719–1726.

[8] HOLESOVSKY, F., NOVAK, M., LATTNER, M., VYSLOUZIL, T. (2013). Machining and its Influence to Surface Quality of Machine Parts. In: *Key Engineering Materials*, Vol. 581, pp.354–359. TTP. Switzerland.

[9] HUSSAIN, S.A., PANDURANGADU, V. & KUMAR, K.P. (2011). Machinability of glass fiber reinforced plastic (GFRP) composite materials. In: *International Journal of Engineering, Science and Technology*, Vol. 3, No. 4, pp.103–118.

[10] JERSÁK, J., VRKOSLAVOVÁ, L. (2013). The influence of process fluids on the properties of the surface layer of machined components. In. *Manufacturing Technology*, Vol. 13, No. 4, pp. 466–473. UJEP, Czech Republic.

[11] JÓZWIK, J., KURIC, I., SÁGA, M., LONKWIC, P. (2014). Diagnostics of CNC machine tools in manufacturing process with laser interferometer technology. In: *Manufacturing Technology*, Vol. 14, No. 1, UJEP, Czech Republic

[12] KASINA, M., VASILKO, K. (2012). Experimental verification of the relation between the surface roughness and the type of used tool coating. In: *Manufacturing Technology*, Vol. 12, pp. 27–30. UJEP, Czech Republic

[13] KOCMAN, K. (2011). Application of magnetic correlation analysis on the choice and correction of cutting parameters for automated manufacturing systems. In: *Manufacturing Technology*, Vol. 11, pp. 28–32. UJEP, Czech Republic

[14] LEGUTKO, S., KROLCZYK, G., KROLCZYK, J. (2014). Quality evaluation of surface layer in highly accurate manufacturing. In: *Manufacturing Technology*, Vol. 14, No. 1, pp.50–56. UJEP, Czech Republic

[15] MIROSLAV, M., PETR, V. (2012). Abrasive wear effect on Polyethylene, Polyamide 6 and polymeric particle composites. In: *Manufacturing Technology*, Vol. 12, pp. 55–59. UJEP, Czech Republic

[16] PECAT, O., RENTSCH, R., BRINKSMEIER, E. (2012). Influence of milling process parameters on the surface integrity of CFRP. In: *Procedia CIRP*, Vol. 1, pp. 466–470.

[17] TETI, R. (2002). Machining of Composite Materials. In: *CIRP Annals - Manufacturing Technology*, Vol. 51, pp.611–634.

[18] UHLMANN, E. ET AL. (2014). Machining of Carbon Fibre Reinforced Plastics. In: *Procedia CIRP*, Vol. 24, pp. 19–24.

[19] VARGA, G., KUNDRÁK, J. (2013). Effect of Environmentally Conscious Machining on Machined Surface Quality. In: *Applied Mechanics and Materials*, Vol. 309, pp. 35–42.

[20] WANG, Y.G. et al. (2011). Cutting Performance of Carbon Fiber Reinforced Plastics Using PCD Tool. In: *Advanced Materials Research.* Vol. 215, pp. 14–18. TTP. Switzerland.

Paper number: M20162

Review of Processing Technologies for Spent Zinc Batteries

Katarína Blašková, Jarmila Trpčevská, Tomáš Vindt
Faculty of Metallurgy, Technical University in Košice, Letná 9, 042 00 Košice. Slovak Republic. E-mail: katarina.blaskova@tuke.sk, jarmila.trpcevska@tuke.sk, tomas.vindt@tuke.sk

This paper deals with the possibility of spent portable batteries treatment with the aim of zinc recovery. Perspective of pyrometallurgical and hydrometallurgical process is described. Samples of zinc based portable batteries were submitted under the investigation. Aim of the work was to find the best conditions for zinc recovery. Experimental work focused on hydrometallurgical process was conducted. Results have shown 100 % zinc recovery

under these conditions: leaching in medium 2 M $(NH_4)_2CO_3$, addition of 20 ml of NH_4OH as reductant, leaching temperature 20°C, within 10 minutes.

Keywords: spent zinc batteries, hydrometallurgy, leaching.

1 Introduction

Batteries have become a preferred portable energy source for electronic devices including mobile phones, cameras, laptops, computers, etc., because of diverse favorable characteristic such as low weight, high energy density, good performance, and so on. Because of wide application of electronic products, the spent portable battery output has rapidly risen. It has resulted in the generation of considerable quantities of discarded waste [1]. Spent portable batteries contain various valuable metals such as zinc, nickel, cobalt, lithium and others. Because of toxic heavy metals content and corrosive electrolytes, batteries are classified as hazardous solid wastes. Recycling of valuable metals from batteries helps reduce environmental contaminations impact as well as the resource shortage [2,3].

There are several treatment routes proposed in order to recycle the metal based wastes. They are divided into three processes: Pyrometallurgical, hydrometallurgical and a mixed of both [4]. Currently, both pyrometallurgical and hydrometallurgical methods have been used in the recycling of spent batteries. The essence of pyrometallurgical treatment is recovering materials by using high temperatures. The process itself is based on extraction and purification of metals by processes involving the application of heat. When dealing with zinc based batteries, evaporation and consequent condensation of recovering metal is conducted. Process is followed by concentrating of additional agent in the rest [5]. In contrast, hydrometallurgical routes are commonly found more economical and efficient than pyrometallurgical ones. Hydrometallurgy requires a pretreatment to ensure leaching process of black powder (separated active mass from crushed and milled batteries) followed by metal recovery from the solution in the most effective way. Recycling through hydrometallurgy basically consists of the acid or base leaching of scrap to put the metals in a solution. Once in a solution, metals can be recovered by various methods [6].

Pyrometallurgical pros and cons [7]:

- \+ High efficiency of metal recovery
- \+ Desirable for big amount of batch
- \+ Relatively simple process.
- \- High investment and operating costs
- \- High energy consumption to ensure the melting process
- \- Dust generation and gas emission
- \- The need to ensure the detention of gas cleaning system
- \- Single devices are intended only for a particular metal, it is not possible to obtain various types of metal in a single device
- \- Profitability of process (necessity of a bigger amount of batch, which is quite difficult to obtain in every country, even in Slovakia for instance).

Hydrometallurgical pros and cons [7]:

- \+ Lower energy consumption for the operation
- \+ Lower initial investment costs
- \+ Zero air pollution
- \+ High purity metal production
- \+ Simple transport of liquid based commodities by pipelines
- \+ Flexibility of process, possibility of adapting for a small batch.
- \- Pretreatment to ensure leaching process
- \- Problem with spent solutions after leaching - corrosive environment
- \- Big amount of waste water
- \- Aggressive used chemicals (acids, alkali).

There are two types of zinc based batteries - zinc-carbon battery and alkaline battery. Zinc-carbon batteries have a carbon rod in contact with carbon and MnO_2 as cathode and a zinc case as anode. A paste of NH_4Cl and $ZnCl_2$ is the acid electrolyte. On the cylindrical cell the zinc electrode is usually recovered with a stainless steel jacket. A plastic or paperboard separator and an asphalt seal are usually present [8-11]. Alkaline batteries were developed after the zinc-carbon and work on the similar principles. These are usually composed of a brass rod in contact with powdered zinc as anode and a steel case in contact with carbon and MnO_2 as cathode. A paste of KOH is used as alkaline electrolyte (pH ~ 14). These batteries have a stable voltage, higher energy density and higher resistance than Zn – C batteries [8-12]. A mixture of anode, cathode and electrolyte material is called a black powder or active mass. The composition of black powder is dependent on type of spent batteries.

2 Experimental material and procedure

For the purpose of research, a sample of spent portable batteries was obtained from collected spent zinc batteries. After mechanical treatment 3 kg of black powder was prepared. Fig. 1 and Fig. 2 show individual parts of zinc-carbon and alkaline batteries after manual dismantling. Leaching experiments were realized using various conditions: concentration of leaching medium, temperature, and time of leaching. Based on experimental results the optimal conditions for selective zinc leaching were determined.

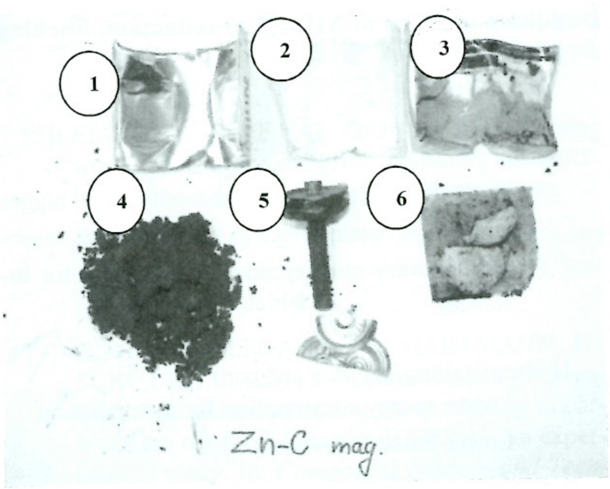

Fig. 1 *Zn-C battery consist of metal cover (1), plastic foil (2), $ZnCl_2$, resp. NH_4Cl (3), mixture of C, Mn oxides (4), graphite rod (5) and separation paper (6).*

Black powder sample was analyzed by AAS (atomic absorption spectrometry) and by XRD analyzer (X-ray diffractometer PANalytical X'pert PRO MPD), as shown in Tab. 1 and Tab. 2.

According to the Tab. 1, black powder contains almost 20 % Zn, 23 % Mn and approximately 18 % Cl.

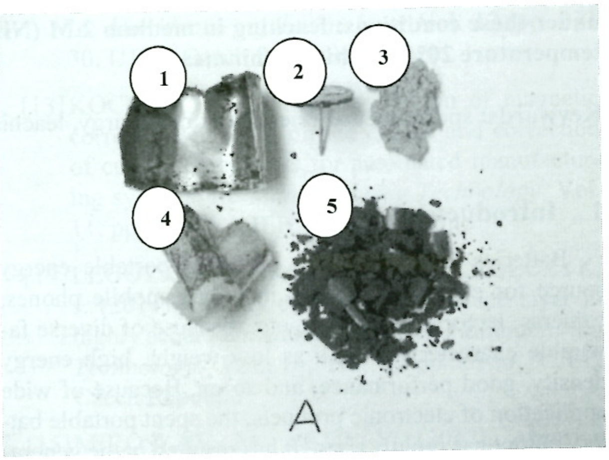

Fig. 2 *Alkaline battery consist of metal cover (1), nickel-coated rod (2), Zn oxides, electrolyte (3), separation paper (4), and mixture of C, Mn oxides (5).*

Tab. 1 *Chemical analysis of black powder*

Element	Amount [%]
Zn	19.68
Mn	23.05
Fe	0.88
K	0.93
Cl	17.71

Tab. 2 *Phase composition of black powder*

Ref. Code	Score	Compound Name	Chemical Formula
00-048-1066	37	Zinc Hydroxide	$Zn(OH)_2$
00-036-1451	32	Zinc Oxide	ZnO
00-036-0791	16	Potassium Hydroxide Hydrate	KOH ! H_2O
00-007-0155	16	Zinc Chloride Hydroxide Hydrate	$Zn_5(OH)$ $8Cl_2$! H_2O
00-039-0697	11	Potassium Oxide	KO_2
00-028-1468	9	Zinc Manganese Oxide	$ZnMn_2O_4$
00-022-0720	6	Manganese Chloride	$MnCl_2$
00-042-1316	4	Manganese Oxide	MnO_2
00-023-0064	1	Carbon	C

As shown in Tab. 2, XRD phase analysis confirms presence of zinc in phase as $Zn(OH)_2$, ZnO, $ZnMn_2O_4$ a $Zn_5(OH)_8Cl_2.H_2O$. The presence of mentioned phases was confirmed also by *L. R. S. Veloso and al.* [13], *I. De Michelis and al.* [14], *de Souza and al.* [15] *a. Freitas and al.* [16].

3 Experimental results

With purpose to achieve a maximum zinc extraction, series of experiments where performed as it is shown in Tab. 3. The best achieved results are depicted in Fig. 3.

Tab. 3 *Summarization of leaching experiments*

Medium	Reductant [ml]	Concentration of medium [M]	Temperature[°C]	Leaching time [min]
$(NH_4)_2CO_3$	-	1, 2, 3	20	60
	-	1, 2, 3	40	60
	-	1, 2, 3	60	60
$(NH_4)_2CO_3$	10 ml NH_4OH	2, 3	20	60
	20 ml NH_4OH	2, 3		60

Tab. 4 *The result of XRD phase analysis of the solid residue after leaching.*

Ref. Code	Score	Compound Name	Scale Factor	Chemical Formula
00-025-0284	33	Carbon	0.730	C
01-071-2499	22	Zinc Manganese Oxide	0.706	ZnMn2O4

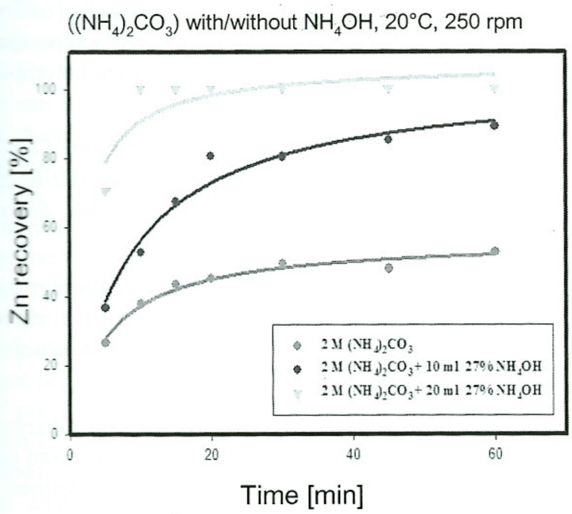

Fig. 3 *Kinetics curves of zinc extraction at temperature of 20 °C in 2 M $(NH_4)_2CO_3$ with and without addition of NH_4OH.*

It was determine that the amount of leached zinc in ammonium carbonate medium depends on both concentration and leaching time. Effect of temperature was negligible. The use of concentrated ammonium carbonate (3 M) at temperature of 20 °C results in zinc leaching (64 %). It can be seen clear increase of zinc recovery (89 %) after adding 10 ml of NH4OH as it is shown in Fig. 3. Addition of 20 ml of agent led to 100 % Zn extraction.

After leaching of black powder the solid residue was submitted to XRD analysis. The result is shown in Tab. 4.

XRD analysis showed that the Zn in solid residual is in form of $ZnMn_2O_4$ compound also called hetaerolite. It follows that Zn leached out from the black powder into the solution from the ZnO a $Zn(OH)_2$ phases. Sample was submitted to annealing at temperature of 600 °C, 700 °C and 850 °C. The sample after annealing can be seen in Fig. 4. The temperature of 850 °C led to decomposition of hetaerolite phase. After the decomposition ZnO and MnO phases were determined by XRD analysis as showed in Tab. 5.

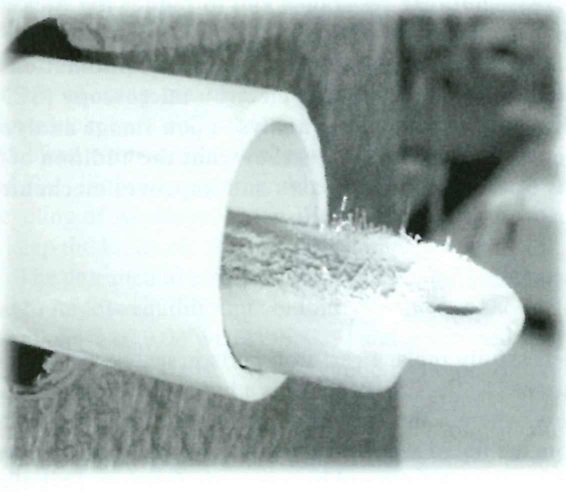

Fig. 4 *Annealed sample*

Tab. 5 *The results of XRD phase analysis of annealed sample.*

Ref. Code	Score	Compound Name	Scale Factor	Chemical Formula
01-075-0625	60	Manganese Oxide	0.727	MnO
00-026-1077	46	Carbon	0.487	C
01-079-0208	22	Zinc Oxide	0.081	ZnO
00-006-0540	13	Manganese Oxide	0.058	Mn_2O_3

4 Conclusion

The performed researches confirm the applicability of ammonium compounds for the leaching of zinc-bearing waste materials. It was examined the influence of a number of parameters on the process of leaching. The optimization of the leaching process, carried out under laboratory conditions allowed to determine the parameters such as time, temperature, concentration of $(NH_4)_2CO_3$, amount of NH_4OH addition as a reductant, at which the process takes place at the maximum efficiency. The optimal conditions for selective Zn extraction seems to be leaching in 2 M $(NH_4)_2CO_3$ with addition of 20 ml 27 % NH_4OH at temperature 20 °C, leaching time 10 minutes The obtained results show that it is possible to reduce the zinc content in the black powder to less than 1% by suggested hydrometallurgical process. The solution after leaching process and suitable subsequent treatment can become a source of valuable metal.

Acknowledgements

This work was supported by a grant from the Slovak National Grant Agency under the VEGA Project 1/0425/14.

References

[1] YANG, L., and al. (2015). Recovery of Co, Mn, Ni, and Li from spent lithium ion batteries for the preparation of LiNixCoyMnzO2 cathode materials, *Ceramics International*, Volume 41, 11498-11503.

[2] YANG, Y., and al. (2015). Thermal treatment process for the recovery of valuable metals from spent lithium-ion batteries, *Hydrometallurgy*.

[3] NOGUEIRA, C. A., MARGARIDO, F. (2015). Selective process of zinc extraction from spent Zn-MnO2 batteries by ammonium chloride leaching, *Hydrometallurgy*, Volume 157,13-21.

[4] ROSSINI, G., BERNARDES, A. E. (2006). Galvanic sludge metals recovery by pyrometallurgical and hydrometallurgical treatment, *Journal of Hazardous Materials*, Volume 131, 210-216.

[5] SAYILGAN. E. (2009). A review of technologies for the recovery metals from spent alkaline and zinc-carbon batteries, vedecký výskum, *Hydrometalurgia*, 97, 158 – 166.

[6] ESPINOSA, D., BERNARDES, A. (2004). An overview on the current processes for the recycling of batteries, *Journal of Power Sources*, 135, 311-319.

[7] SAYILGAN. E. (2009) A review of technologies for the recovery metals from spent alkaline and zinc-carbon batteries, *Hydrometalurgy*, 97, 158 – 166.

[8] BERNARDES, A., ESPINOSA, D. (2004). Recycling of batteries: a review of current processes and technologies, *Journal of Power sources*, 130, 291-298).

[9] Batérie [online]. Dostupné na ineternete:http://batteryuniversity.com/learn/article/primary_batteries [citované 18.10. 2013].

[10] ORÁČ, D., VINDT, T. (2014). *Druhotné suroviny a odpady*, návody na cvičenia, Košice, IBAN 978-80-553-1644-4.

[11] CARSTEN, H. (2014). Recovery of Zinc from Spent Batteries by the Treatment in a Shaft Furnace, *Erzmetall – World of Metallurgy*, 67/2014 No.4, GDMB Verlag GmbH, ISSN 1613-2394.

[12] Division of primary and secondary cells [online]. Available on the ineternet: http://www.separujod-pad.sk/index.php/obcan/ako-separovat/baterie-aakumulatory.Html.

[13] VELOSO, L. a kol. (2005). Development of a hydrometallurgical route for the recovery of zinc and manganese from spent alkaline batteries, *Journal of Power Sources* 152, 295 – 302.

[14] DE MICHELIS, I. a kol. (2007). Recovery of zinc and manganese from alkaline and zinc carbon spent batteries, vedecký výskum, *Journal of Power Sources* 172, 975 – 983.

[15] MARTA DE SOUZA, C. a kol. (2001). Characterization of used alkaline batteries powder and analysis of zinc recovery by acid leaching, *Journal of Power Sources* 103, 120 – 126.

[16] FREITAS, M. a kol. (2007). Recycling manganese from spent Zn – MnO2 primary batteries, Journal of Power Sources 164. 947 – 952.

Paper number: M20163

The Impact of Sr Content on Fe - Intermetallic Phase's Morphology Changes in Alloy AlSi10MgMn

Kamil Borko, Eva Tillová, Mária Chalupová
Faculty of Mechanical Engineering, University of Žilina, Univerzitná 8215/1, 010 26 Žilina. Slovak Republic. E-mail: kamil.borko@fstroj.uniza.sk

The effect of modification (with AlSr10) on the microstructure of hypoeutectic AlSi10MgMn cast was systematically investigated. The samples were studied in as cast state without Sr (0 % Sr) and after modification (0.05 % Sr; 0.1 % Sr and 0.15 % Sr). Iron is added to Al-Si alloy to increase hot tear resistance and to reduce die sticking, but can change the solidification characteristics by forming pre- and post-eutectic β-Al5FeSi phase or other Fe-rich phases, which can be very detrimental to the mechanical properties of the final cast part. A combination of different analytical techniques (light microscopy upon black-white etching; scanning electron microscopy (SEM) upon deep etching and energy dispersive X-ray analysis (EDX); quantitative phase analyse upon Image analyzer NIS Elements 3.0) were therefore been used for the microstructure study. The results show that the addition of Sr into AlSi10MgMn cast alloy modified eutectic silicon as well as Fe-intermetallic phases and improves mechanical properties (ductility, strength).

Keywords: aluminium cast alloy, microstructure, Fe-rich phases and morphology

1 Introduction

Aluminium alloys with high silicon contents exhibit high strength, low thermal expansion and high wear resistance. These qualities, together with their excellent castability and reduced density, make these alloys very interesting for the automotive industry where they can successfully replace cast iron parts in heavy wear applications [1, 2]. AlSi10MgMn is a hypoeutectic aluminium alloy wherein the aluminium solid solution precipitates from the liquid as the primary phase in the form of a dendritic network followed by a eutectic reaction. This alloy contains about 50 volume % eutectic phases [3].