TRANSFORMING WASTE NI-MH BATTERY ELECTRODES TO NICKEL BASED ALLOYS BY NOVEL AND SUSTAINABLE PYROMETALLURGICAL RECYCLING METHODS

[1]PRAVAS RANJAN BEHERA, [2]RIFAT FARZANA, [3]RAVINDRA RAJARAO, [4]VEENA SAHAJWALLA

PhD candidate, Research Associate, Research Associate, Scientia Professor
E-mail: p.behera@student.unsw.edu.au, r.farzana@unsw.edu.au, r.rajarao@unsw.edu.au, veena@unsw.edu.au

Abstract— Recovery of valuable metals such as nickel, and synthesis of alloys (Ni-Co and Fe-Ni) from waste Nickel-metal hydride (Ni-MH) batteries is a major area of focus and interest in this present work. Novel, green, and sustainable techniques, such as combination of two waste streams (e-waste plastics as a potential carbon source and waste Ni-MH batteries) and hydrogen plasma smelting were adopted to synthesize industry grade nickel-cobalt alloy and ferro-nickel alloy. Reduction of nickel oxide present in waste Ni-MH battery, using e-waste plastic, facilitated 99% nickel-cobalt alloy with ICP-OES and XPS analysis corroborating the results. Usage of e-waste plastic, as a potential alternative to conventional carbon, observes the gas-based reduction of nickel oxide. Hydrogen plasma smelting of nickel oxide in a maintained reducing ambience of argon and hydrogen flow rate (1:1) experiences the rapid reduction reaction (1800-2000°C), duly complemented by three forms of hydrogen (atomic, molecular, and ionic). The formation of ferro-nickel occurs within 15 min with Fe (66 wt%), Ni (31 wt %) and Co (2%) that are close to the industry standard. Moreover, hydrogen plasma smelting pushes rare earth elements (present in cathode of Ni-MH battery) to slag phase (La: 24 wt%, Ce: 11 wt%, and Nd: 7 wt%) in the form of oxides without contaminating the product phase. Characterisation analysis of product and slag phase were performed using XRD and ICP-OES techniques. These scientific recovery techniques put forth a promising eco-friendly and sustainable solution to utilise waste resources in a befitting way, thus recovering valuable metals and alloys and safeguarding the environment at the same time.

Index Terms— waste Ni-MH battery, sustainability, hydrogen plasma, nickel alloy, e-waste plastic

I. INTRODUCTION

A rapid growth in economies around the world brings in quick technological changes and innovations that go in tandem with the production of several electronic devices, gadgets, and products that influence the life style. However, there is a generation of huge pile-up of electronic waste (e-waste) which throws a blend of social and environmental challenge for the researchers worldwide. The production figure of e-waste touched 42 million tonnes in 2014 which is further anticipated to escalate to 50 million tonnes by end of 2018 (Balde et al., 2014; Rajagopal et al., 2016). Spent batteries also contribute a good part of e-waste with 0.3 million tonnes of waste batteries form the total toxic materials that emanate from e-waste (Babu et al., 2007). As per the report by Freedonia, 2015, the global demand of battery will see a growth by 7.7% every year to reach a staggering $120 billion in 2019. In Australia alone, 345 million portable batteries enter the market every year with nearly two-thirds of waste batteries dumped in the landfill (Australian Battery Recycling Initiative, 2013). Owing to the properties, namely energy density, charge-discharge cycle efficiency, design flexibility, rechargeable batteries (Nickel metal hydride (Ni-MH) and Lithium ion) are preferred for broad range of applications. Ni-MH battery is the first choice for power equipment and portable electronics with 57% of the usage seen in commercial hybrid electric vehicles (Fetcenko et al., 2015; Erika et al., 2016). The rate of consumption leads to an alarming situation of generation of waste batteries that cause a potential injury to the human health and environment alike (Xara et al., 2015). Recycling of waste Ni-MH batteries brings the possible solution to tackle the situation by recovering the valuable elements present and also protecting the damage caused to the environment. The normal composition of a Ni-MH battery is Ni (36-42%), Mischmetal (8-10%) containing rare earth elements (REEs), and Co (3-4%) (Muller and Friedrich, 2006). Furthermore, the recent reduced supply of REEs by China has brought quite a stir in the world market to meet the overall demand (Leotaud, 2016). The present work covers the innovative pyrometallurgical techniques to synthesize valuable Ni-based alloys and prepare slag rich in rare earth oxides (REOs). The table 1 presented below summarizes the adopted pyrometallurgical techniques till date to recycle waste Ni-MH batteries worldwide.

Table 1

Year and Reference	Process type	Highlights
1992, INMETCO	Electric Arc Furnace and distillation	Ni recovered is considered suitable for steel industry. However, the slag containing rare earth oxides necessitates further refining techniques
2002, SNAM	Pyrolysis, distillation, and refining	Ni is the only target metal recovered
2006, Muller et al.	DC Electric Arc Furnace and separation	Ni-Co alloy formation was feasible with easy

		separation from the slag containing rare earth oxides
2013, Kuzuya et al.	Chlorination roasting and leaching	Rare earths were recovered first through vaporisation with the residue rich in Ni and Co
2015, Jiang et al.	Selective Redox process and reducing with hydrogen in vacuum furnace	Ni-Co alloy obtained was of highest purity suitable for direct usage in making AB5 hydrogen storage alloys

The present work explores two different waste Ni-MH battery recycling techniques: (a) Use of e-waste plastic as a promising carbon alternative to reduce nickel oxide present in the positive electrode of the Ni-MH battery in a quick span of 15 mins (b) Use of hydrogen as an alternative reductant in plasma environment to synthesize ferro-nickel alloy and prepare a slag rich in REOs. The novelty of two techniques is bringing together two big waste streams (waste Ni-MH batteries and e-waste plastic) and ruling out the necessity of using a fluxing agent to prepare REOs in hydrogen plasma smelting reduction process. Both the raw material and product and slag phases were analysed through various characterisation techniques (XRD, XRF, and ICP-OES). The metal phase obtained through e-waste plastic reduction of positive electrode of waste Ni-MH battery confirmed the purity of the alloy ~91% Ni and ~7% Co while hydrogen plasma smelting reduction facilitated synthesis of ferro-nickel alloy (66Fe-31Ni-2 Co wt%) from positive electrode of waste Ni-MH battery and recovery of 42 wt% Ni and 51 wt% Fe from negative electrodes with REOs in the slag phase (La: 24 wt%, Ce: 11 wt%, and Nd: 7 wt%).

II. EXPERIMENTAL

Waste Ni-MH batteries and e-waste plastics (Acrylonitrile Butadiene Styrene (ABS) + Polymethyl methacrylate (PMMA)) were procured from the UNSW recycling site and separated manually to identify the positive and negative electrodes of the battery. A Rocklabs Ring mill was used to grind the electrodes to powder form and reducing the e-waste plastics to -2mm size by using a Knife mill. The approach followed in two recycling techniques is as follows:

The reduction experiment was performed in a high-temperature horizontal tubular furnace (as shown in figure 1) operated by 1550°C with a constant Ar supply (1 litre/min). Before carrying out the reduction experiment, pellets were prepared by considering a stoichiometric amount of e-waste plastic and positive Ni-MH electrode in 1.5 g scale in a uniaxial hydraulic press (3 bar, 60°C, 2 min). A time variation (2, 4, 6, 8, 15 min) was followed to study the reduction process. Post every experiment, the samples were moved from the hot zone to cold zone and kept for 10 mins cooling under Ar purging. Additionally, degradation feature of e-waste plastic with/without positive electrode was studied by real time Infrared gas analyser (IR, ABB, Advanced Optima Series, AO2020). Characterisation of the product and slag phase was carried out using X-ray powder diffraction (XRD), Inductive coupled plasma optical emission spectroscopy (ICP-OES), X-ray photo electron spectroscopy (XPS) and Field emission scanning electron microscopy (FE-SEM) and Energy Dispersive X-ray spectroscopy (EDS).

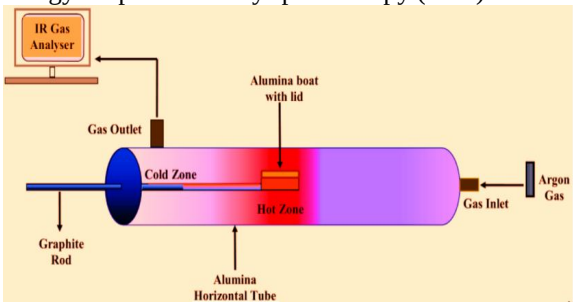


Figure 1. Horizontal tubular furnace

The smelting reduction experiment using hydrogen in a plasma reactor (as shown in figure 2) was carried out in a setup that comprises of a water chiller, power control unit, and gas regulators. The reactor consists of a plasma torch as the cathode, a water-cooled copper sample holder as the anode, and an electromagnetic coil beneath the copper sample holder for bath agitation. Individual powdered positive and negative electrodes were taken in 50g scale, incorporating a stoichiometric amount of iron oxide powder for ferro-nickel alloy synthesis. Ar was passed into the furnace which takes care of the explosive trait of hydrogen and is also known as a carrier gas for plasma expansion. Ar and H_2 were passed in 1:2 ratio during the reduction process with current varying from 90 amp to 130 amp in 2 min gap. After the reduction was carried out for 15 min, the product and slag phases were cooled down for 30 min under Ar purging. The product and slag collected and separated were weighed and characterised by XRD, ICP-OES, XPS, FE-SEM and EDS analytical techniques.

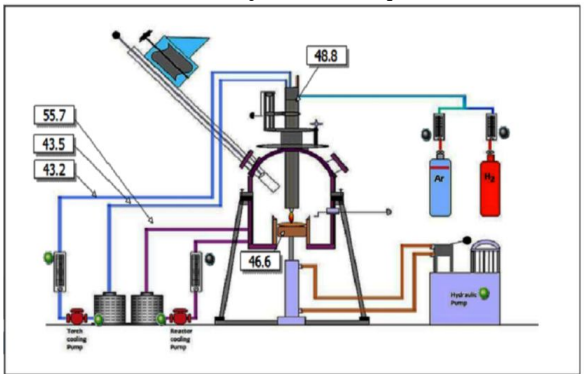


Figure 2. Schematic of the hydrogen plasma smelting reactor

III. RESULTS AND DISCUSSION

Occurrence of nickel in anode (65.64%) and cathode (30.67%) in the form of oxide is confirmed by the XRF analysis. The cathode material contained rare earth elements, such as lanthanum (14.10%) and cerium (6.29%) as reported by semi-quantitative XRF analysis results. XRD spectrum of both electrodes is shown in figure 2 which indicates nickel hydroxide as the dominant phase in anode at 2θ values ~38° and ~90° whereas presence of alloys lanthanum-nickel (reference code: 00-053-0618) and cerium-cobalt (ICDD: 04-00102710) are seen in the cathode. Analysis of the e-waste plastic used in this study by LECO carbon analyser and CHNS indicated the presence of carbon (~84%), hydrogen (~8%), nitrogen (~5%), and sulphur (~0.09%).

The reduction reaction of nickel oxide with that of the e-waste plastic is observed to be mostly gas based as illustrated in figure 3. The evolution of volume percentage of carbon monoxide gas controls the reduction reaction while a very small contribution towards reduction of nickel oxide by carbon dioxide and methane is seen in the figure. While carbon monoxide evolves higher compared to other two gases (which dwindle almost within 1 min when the feed material is placed at the hot zone), it continues to be present in the furnace through a linear profile after 14 min, thus completing the reduction.

The progress of reduction, commencing from the hot zone and reaching completion within 15 min is evident from the figure 4 which highlights the evolution of total oxygen (in moles) in the furnace. It is seen that the profile of oxygen evolution follows the same curve as that of carbon monoxide evolution, thereby confirming participation of carbon monoxide as the dominant reductant in this gas-controlled reduction of nickel oxides.

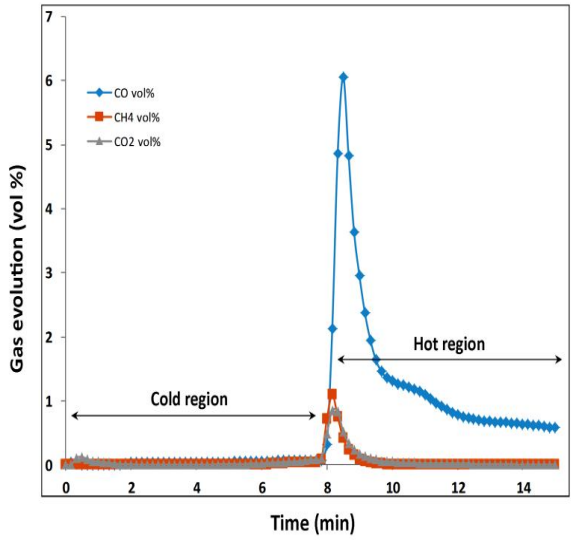


Figure 3. Gas evolution during reduction of nickel oxide with e-waste plastic at 1550°C

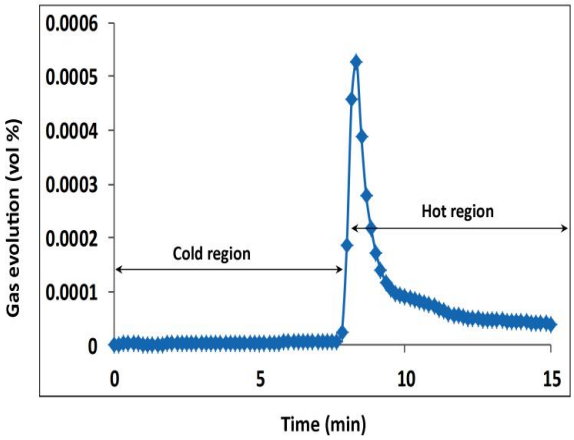


Figure 4. Total oxygen evolution during the reduction of nickel oxide

The product cobalt-nickel alloy (ICDD:04-021-8175), having cubic crystal system, is found to occur at (111), (200), (220), and (311) with respective 2θ values 52°, 61°, 91°, and 114° respectively by using plastic for 15 min reduction time (shown in figure 5). However, 8 min of the reduction time gives cobalt-nickel alloy with the formula Co_3Ni, occurring at different 2θ values (52°, 61°, 92°, and 115°) on the same orientation planes as in 15 min. Considering the 6 min reduction reaction in both plastics, the cobalt-nickel alloy phase continues to have the highest peak at 52°. The XRD patterns, as seen in the 4 min reduction reaction using both plastics, indicate nickel (ICDD:04-010-6148) appearing in the product phase instead of cobalt-nickel alloy. With cubic crystal system, nickel shows lattice parameters 3.51Å and occurs on the same planes as cobalt-nickel alloy with the same 2θ values. Patterns for the product obtained from 2 min reduction reaction, using both plastics, show presence of cobalt-nickel as the oxide phase and nickel oxide. Additionally, the detection of the nickel in 2 min XRD pattern confirms the reduction reaction starts faster and proceeds to completion in 15 min. The corresponding slag obtained shows some unreduced oxides of iron, silica and a compound formed between zinc, nickel and silicon. This could be attributed to the presence of impurities in the e-waste plastic and electrode material. Furthermore, the metal content and the relevant purity was analysed through ICP-OES technique which confirmed >98% of Ni-Co alloy occurring together.

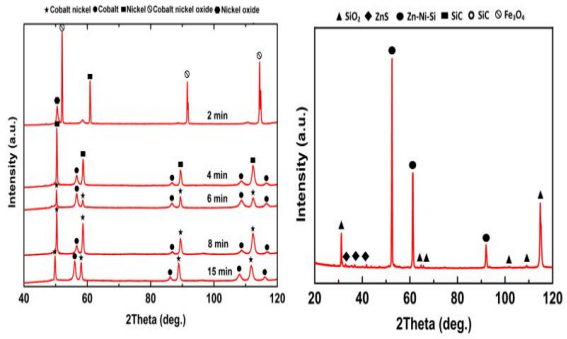


Figure 5. XRD spectra of metal alloy and slag

In the research investigation of using another reductant apart from carbon, hydrogen smelting of both electrodes of spent Ni-MH battery was carried out. Hydrogen, as a reductant, was quick to reduce iron and nickel oxides, forming ferro-nickel alloy in a similar timespan of 15 min as observed in case of e-waste plastic. XRD spectrum of the ferro-nickel alloy (shown in figure 6 (a) and (c)) confirms its presence in the exact cubic lattice system (ICDD:03-065-5131) with lattice parameter 3.598Å, prominent peak (111) at 2θvalue ~51°, obtained by using individual electrodes (anode and cathode) as feed materials. Presence of unreduced oxides of nickel and iron in the anode slag and lanthanum oxide in the cathode slag was observed in the XRD spectra obtained in the slags (shown in figure 6 (b) and (d)). Nickel-iron oxide occurring together (ICSD: 084099), iron oxide (ICSD: 082235) and cobalt iron oxide (Reference code: 00-022-1086) were seen in the anode slag. Furthermore, two oxides, namely nickel-iron oxide and cobalt iron oxide are observed to be present in the same crystal plane (311) and cubic lattice with varying respective lattice parameters 8.368 Å and 8.391 Å.

Whereas cathode slag contained lanthanum iron-nickel (ICSD: 084939) present in orthorhombic crystal lattice system, occurring in widely distributed orientation planes (101), (121), (220), (202), and (240) at respective 2θangles ~26°, ~38°, ~47°, ~54°, and ~68°. ICP-OES analysis results conveyed the metal content of the alloy with iron and nickel present in weight percentages 66% and 31% respectively, the grade which is placed pretty close to industrial applications. The ferro-nickel obtained by using cathode as the feed material contains nickel at 42% and iron at 51% with to contamination coming from the rare earth elements.

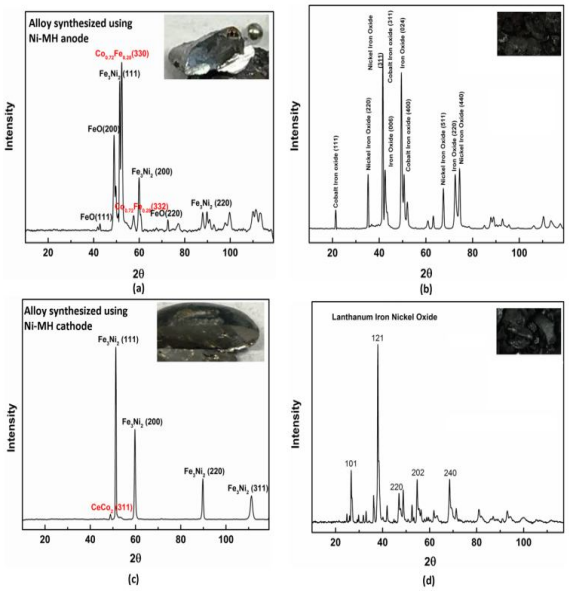


Figure 6. (a) Ferro-nickel obtained using Ni-MH anode and (b) the corresponding slag and (c) Ferro-nickel obtained using Ni-MH cathode and (d) the corresponding slag

CONCLUSIONS

Following conclusions were arrived at through this study:

- Synthesis of nickel-cobalt alloy using an optional carbon source e-waste plastic was made possible with metal content in the alloy reaching almost 98%.

- A green methodology to synthesize ferro-nickel alloy of high purity (65Fe-30Ni) could be made possible through hydrogen plasma treatment of waste Ni-MH batteries.

- Hydrogen, as a faster reductant, along with high heat generated by plasma made the reaction quick, pushing rare earth elements to the slag, without interfering in the product phase.

- Both the reduction mechanisms (by e-waste plastic and by hydrogen plasma) exhibited the reduction proceeds to completion within 15 min.

- These novel recycling techniques could reduce burden on the landfill of these waste resources while manufacturing semi-finished alloys.

REFERENCES

[1] Balde, C., Wang, F., Kuehr, R., Huisman, J., 2014. The Global E-Waste Monitor. United Nations University, Germany.

[2] <https://i.unu.edu/media/unu.edu/news/52624/UNU-1stGlobal-E-Waste-Monitor-2014-small.pdf> (accessed on April 2019).

[3] Raman Rajagopal, R., Rajarao, R., Cholake, S., Sahajwalla, V., 2016. Sustainable composite panels from non-metallic waste printed circuit boards and automotive plastics. J. Clean. Prod. 144:470-481.

[4] Babu R, Parande A.K., Basha A.C., 2007. Electrical and electronic waste: a global environmental problem. Waste Manag. Res. 25:307-318.

[5] Australian Battery Recycling Initiative (ABRI). 2013. Global Product Stewardship Council.

[6] <http://www.globalpsc.net/tag/australian-battery-recycling-initiative/page/2/>(accessed on April 2019)

[7] Fetcenko, M., Koch, J., Zelinsky, M., 2015. Nickel-metal hydride and nickel-zinc batteries for hybrid electric vehicles and battery electric vehicles. Advances in Battery Technologies for Electric Vehicles. 6:103-126.

[8] Erika, T., Sebastian, C., Fernando, Z., Veronica, D.,2016. Temperature performance of AB5 hydrogen storage alloy for Ni-MH batteries. Int. J. Hydrogen Energ. 41:19684-19690.

[9] Xara S, Almeida MF, Costa C. Life cycle assessment of three different management options for spent alkaline batteries. Waste Manage 2015;43:460-84.

[10] Muller, T., Friedrich, B., 2006. Development of a recycling process for nickel-metal hydride batteries. J. Power Sources 158: 1498-1509.

[11] Leotaud, V.R., 2016. Rare earths: Battling China's monopoly after Molycorp's demise. Mining.com. <http://www.mining.com/rare-earths-battling-chinas-monopoly-after-molycorps-debacle/> (accessed on April 2019).

[12] Hanewald, R.H., Munson, D.L., Schweyer, D.L., 1992. Processing EAF dusts and other nickel–chromium waste materials pyrometallurgically at Inmetco. Miner. Mater. Process. 11: 169-173.

[13] SNAM. <http://www.snam.com/activites/recycling-snam.php> (accessed on April 2019).

[14] Kuzuya, T., Hirai, S., Sokolov, V.V., 2013. Recovery of valuable metals from a spent nickel–metal hydride battery: Selective chlorination roasting of an anodic active material with CCl_4 gas. Separation and Purification Technology 118: 823-827.

[15] Jiang, Y., Deng, Y., Bu, W., 2015. Pyrometallurgical Extraction of Valuable Elements in Ni-Metal Hydride Battery Electrode Materials. Metall. Mater. Trans. B 46: 2153-2157.

★★★