

RECOVERY OF RARE EARTHS FROM E-WASTE RESIDUES FOR PRODUCTION OF HIGH-PERFORMANCE REE-Mg ALLOYS

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This paper describes first outcomes from the research activities of the REMAGHIC project, funded by EU under program H2020 SPIRE 2015 (Grant Agreement N°680629)¹. The specific target of the project is the recovery of rare-earth elements (REEs) and magnesium from a selection of residues in order to provide critical secondary raw materials to produce magnesium alloys with improved properties and reduced price for several industrial sectors such as the automotive, aeronautic and biomedical industries in particular. The aim is to reduce the European dependency of critical raw materials (REEs and Mg) from non-European countries and to partially mitigate the so-called “Balance Problem”^{2,3}, that is the balance between the demand by the economic markets and REEs in ores. The Balance Problem implicates that the rare-earth industry has to find new applications for REEs that are available in excess. A detailed research carried out at early stage in the project shows that magnesium alloys offer an excellent opportunity to mitigate the Balance Problem.

Three waste residues were selected as potential source of REEs: spent lamp phosphors, cathode ray tube (CRT) phosphors and nickel-metal hydride (NiMH) batteries. Samples from industrial source were characterized by ICP-OES, SEM/EDS and XRD in order to gather information about their chemical and mineralogical composition. The analysis of CRT phosphors showed yttrium in concentration around 15% together with 1% of europium. In regards to lamp phosphor waste, this residue contains significant amounts of Y (6%), La (0.9%), Ce (0.7%), Eu (0.4%), Tb (0.3%) and Gd (0.1%). The electrode active parts (black powder) of the NiMH batteries contain La (13%) and Ce (2%). Recycling of REEs from above residues will generate a supply of lanthanum, europium, terbium, yttrium, cerium and gadolinium. Most of these REEs can also be used in applications different from their recovery source. Lanthanum, cerium and especially yttrium can find new uses in magnesium alloys and, consequently, is the main focus in the REMAGHIC project.

REEs recovery from the selected waste residue is investigated through a combination of different techniques, namely hydrometallurgical processes, solvometallurgical processes, high-temperature molten salts and high-temperature processes.

REEs recovery from the lamp phosphor waste is performed by leaching with H₂SO₄ followed by precipitation with oxalic acid in the HydroWEEE process; the recovered product is a mixed REE oxalate which can be further treated by calcination to obtain a mixed REE oxide.⁴ To verify the possibility of enhancing the REEs leachability (mainly Tb) by hydrometallurgy, a thermal treatment (roasting in the presence of Na₂CO₃) was researched (high-temperature process). Y/Eu separation from the mixed REE oxide was investigated by solvent extraction with the ionic liquid Cyphos IL 101 in thiocyanate form. Regarding the CRT phosphors, HydroWEEE process can also be applied for REE recovery. A thermal pretreatment will here be considered to oxidise the ZnS contained in the CRT powder (ZnS, the host matrix of the green and blue phosphors) to ZnO, thus avoiding H₂S release during the leaching step. The possibility of selectively removing zinc from the roasted CRT phosphors was

investigated by employing acetic acid as leaching agent in the solvometallurgical process; Y and Eu recovery from the leaching residue was then studied by employing methanesulfonic acid. The reduction in the sulfur content of the CRT powder will also be studied through treatment with molten salt processes, which are also promising in terms of REEs enrichment in the solid phase. Several salts mixtures were investigated, such as formate, acetate, carbonate, hydroxide or nitrate salt mixture.

Concerning NiMH batteries, the black electrode powder is treated by a leaching step with HCl; REEs recovery from the leachate is investigated through solvent extraction with ammonium and phosphonium ionic liquids in an solvometallurgical process.⁶ The HydroWEEE process will be tested as well. With the pyrometallurgical method, a metal phase rich in nickel and other minor metallic compounds is obtained, whilst the REEs concentrate in the slag phase as oxides. Molten salt processes are also tested to achieve an enrichment of REEs in the solid phase.

References

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RECYCLING OF RARE EARTHS FROM LAMP PHOSPHOR WASTE: ENHANCED DISSOLUTION OF $LaPO_4:Ce^{3+}, Tb^{3+}$ BY MECHANICAL ACTIVATION

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Introduction

With the promoted use of compact fluorescent lamps (CFLs) and the increasing amount of stockpiled CFL waste, lamp phosphors have become an interesting secondary source for critical metals (Y, Eu and Tb). Phosphors for fluorescent lamps and compact fluorescent lamps are an important application of rare-earth elements (REEs), accounting for more than 30% of the total REE market by value. These phosphors consist of a mix of a red $Y_2O_3:Eu^{3+}$ (YOX), green $LaPO_4:Ce^{3+}, Tb^{3+}$ (LAP) or $CeMgAl_{11}O_{19}:Tb^{3+}$ (CAT), and blue $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) phosphor. Besides the rare-earth bearing phosphors, lamp phosphor waste consists up to 50% of $Ca_{4.86}Mn_{0.10}Sb_{0.04}Sr_{0.004}(PO_4)_3Cl_{0.10}F_{0.90}$ halophosphate phosphor (HALO) which has low intrinsic value and contains no REEs¹.

Most studies focus on the recovery of yttrium and europium from the red phosphor YOX, because these are the elements that are easiest to recover and they represent the highest value in the phosphor waste^{1,2}. Recycling of the green phosphors (LAP, CAT) is also very interesting due to the high concentration of the critical and expensive terbium. However, the green phosphors are much more difficult to dissolve than YOX or