Recovery of rare earth oxides from NdFeB magnet grinding slurries and their reuse in molten salt electrolysis

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Extended abstract

Due to monopoly of China in rare earth metal production the prices for them skyrocketed in 2011 leading the rest of world to start with immediate research in this area to decrease dependency. Although even some European countries have reasonable resources of rare earths [1], the complexity of processes and production of radioactive waste contradict the European standards and hinders the rise of this industry [2]. Nevertheless, another possibility to secure the supply of rare earth elements (REEs) can be seen in recycling of their end products. Most used rare earth metal is neodymium for permanent magnets (NdFeB) in wind turbines and during their production high amount of scrap is made containing high concentration of REEs.

In our study recovery of neodymium, praseodymium and dysprosium in their oxide form from grinding slurries created during shaping process of magnets is the main task. Following, those oxides can be used in molten salt electrolysis in order to directly a master alloy. As the shaping process occurs on high temperature (up to 1000 °C), during which oxygen content in slurries increases [3], cooling agent has to be employed causing carbon contamination. Although the cooling agent is separated from slurries by magnetic separation or a filter system the remaining amount varies between 1-20 wt.-% which hinders direct recycling. Therefore pyrolysis pre-step is necessary in order to remove the cooling agent and to avoid agglomeration of metallic swarfs. Pyrolysis process was conducted in an appropriate batch reactor connected to condensate tanks via exhaust pipes for collecting the volatile products. The tests are done in temperature range of 200 – 650 °C and with different retention times of 15 - 60 min under inert atmosphere. The pyrolysed grinding slurries were analyzed by ICP-OES where moisture and volatile content is determined as well. Such a pretreated material is employed in recycling/melting experiments in order to separate the metal phase (mostly Fe) from RE-oxides in a slag phase. The separation of the phases is based on the high oxygen affinity of REEs [4]. Melting is conducted in a graphite crucible placed in vacuum induction furnace. As the input material of each sample differs in content the melting point was observed and determined optically. Obtained phases were analyzed by X-ray diffraction (XRD) and ICP-OES technique. Furthermore, the influence of oxygen content in input material on phase separation and oxygen uptake in dependence on holding time and temperature was investigated. Such REOs need to be purified by leaching and solvent extraction to reach satisfying quality for molten salt electrolysis. At our Institute molten salt electrolysis of mixed neodymium and praseodymium (didymium) oxides in fluoride based electrolyte is investigated also. The electrochemical technique (chronoamperometry) and in-situ FTIR-spectroscopy are employed for process window determination. Electrolysis is done in closed cell with graphite anode and crucible and tungsten cathode under inert atmosphere. Electrolyte compositions, based on NdF_3-PrF_3-LiF are varied and its influence on metal composition is established. X-ray fluorescence spectroscopy (XRF) is used for alloy analysis.

Results of pyrolysis show that best conditions for this process is temperature of 600 °C and 15 min. retention time during which the amount of cooling agent is reduced below detection limit and

remaining carbon is transformed into a solidified coke [5, 6]. Melting trials resulted in separation of 60-65 % of metallic Fe phase and of about 30 % of slag (REOs) phase which are highly influenced by carbon and oxygen content in starting material. If the oxygen content was below 7 wt.-% phase separation was not successful, compared to material with higher oxygen content (Figure 1 a, b) leading to extraction > 99 % of REOs [7]. Thermal oxidation process was possible resulting in >7 wt.-% oxygen uptake after 1.5 h at a temperature of 550 °C [8].

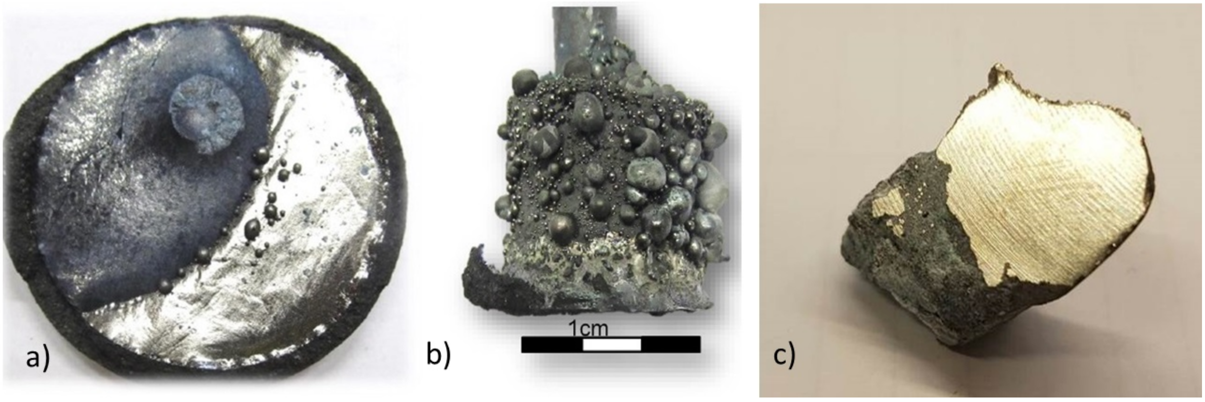

Figure 1: a) separated phases after melting; b) agglomeration with melt droplets [7] c) didymium alloy obtained by molten salt electrolysis [9]

Electrolysis trials revealed that alloy composition is directly influenced by electrolyte composition, i.e. activity concentration is transferred to composition. Increase in praseodymium content in electrolyte lead to higher praseodymium content in alloy, where obtained alloy had high purity > 99 % (Figure 1 c). Optimal anodic and cathodic are determined to be 0.46 and 4.5 A/cm^2, respectively.

Keywords: rare earths elements, grinding slurries, recycling, molten salt electrolysis

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