Recovery of rare earth elements from NdFeB based grinding slurries

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Abstract

Since there is a constantly increasing need of rare earth elements (REE) for high tech applications combined with the supply risk of those elements from primary resources, strategies for recovering REE from scraps are essential for providing a stable supply. To this day, more than 95% of REEs needed in Europe are imported from China due to a lack of primary resources which are economically recoverable, as well as missing recycling concepts for the arising scraps.

Due to their high saturation magnetisation and high magnetic polarization, neodymium-iron-boron magnets are among the strongest available permanent magnets. They can be found in various applications such as hard disc drives, speakers, dc motors or wind turbines. The high amount of REEs contained in these magnets contributes to the value of residues which occur during manufacturing. One of the most common residues in production is the grinding slurry or grinding sludge which arises within the grinding process of the sintered magnets. Up to 5 % of the magnetic alloy end up in this sink. In this investigation, the possibility of a pyrometallurgical treatment of such grinding slurries should be determined. Since REEs have a high oxygen affinity, the main focus of the pyrometallurgical treatment is to separate REEs from the iron by oxidizing and enriching them in a slag phase. The iron remains in a metal phase combined with other accompanying elements such as cobalt and boron. The oxygen needed for the oxidation is already contained in the raw material, as well as some amount of carbon.

1 Introduction

NdFeB grinding slurries are the residual output of grinding as shaping process step in the production process of sintered NdFeB magnets. The recovery of the metallic swarfs contained in the grinding slurries may lead to a reduced demand in primary raw materials like the rare earth elements neodymium, praseodymium and dysprosium. The named REE are essential components in the magnet alloy and account for up to 30 weight percent (wt.-%) in the alloy. In order to recycle the metallic swarfs included in the grinding slurry, it is necessary to perform a pre-treatment before a pyrometallurgical process takes place.

1.1 Production of NdFeB magnets

The conventional production route for sintered NdFeB magnets consists of vacuum induction melting, followed by crushing and milling as well as pressing and sintering of the magnet material. Nd-Fe and Fe-B master alloys are used as input material. The process route is shown in Figure 1.

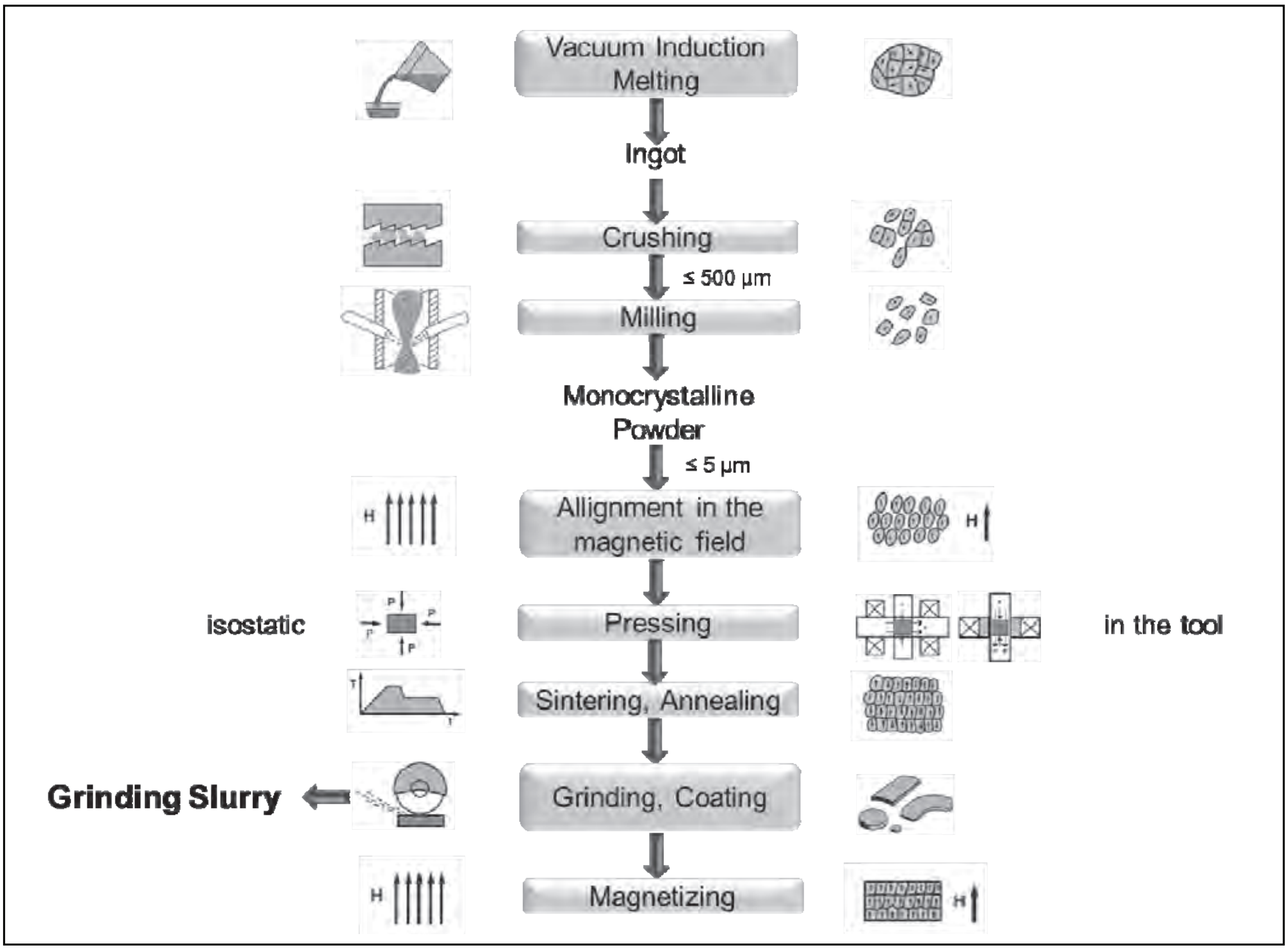

Figure 1: Flow sheet for the production of NdFeB magnets [1],[2],[3]

The obtained ingot from melting of the alloys is crushed and grinded to < 5 µm, before the monocrystals can be aligned in a magnetic field. Subsequently, the pressing and sintering process takes place to adjust the favoured texture. During the next step, the material is grinded into its final shape. Within this process, the grinding slurries, which are the main issue of this paper, occur. Finally the material is magnetized. [2][3]

1.2 Characterization of NdFeB based grinding slurries

Due to the necessary application of cooling agents in the grinding process, the grinding slurries are a mixture of metallic swarfs, abrasions of the grinding media and a relevant amount of cooling agent as can be seen in Table 1. For the direct circulation of the applied cooling agent, an on-site solid-liquid-separation is applied. Still, the amount of remaining cooling agent in the grinding slurries varies between 1 % and > 20 % depending on the applied method for solid-liquid separation. The most current methods for solid-liquid separation are magnetic separation or filter systems. The amount of cooling agent can be reduced from 30 % to 10 %.

The grinding is usually done with diamond abrasives as the alloy is very hard. The amount of abrasions of the grinding media remaining in the grinding slurry is extremely low. It is considered to be insignificant for the material composition as the main component it may add to the mixture of substances is carbon from the diamond abrasives or its bond.

Table 1: Composition of the slurries directly after grinding

Components	Share	Range of fluctuation
Metallic Swarfs	80 wt.-%	± 10 wt.-%
Cooling Agent (Emulsion)	20 wt.-%	± 10 wt.-%
Abrasion of grinding media	negligible	negligible

While the composition of the machined magnets can be considered as homogenous, the arising slurries have a different composition due to contamination with cooling agent. An exemplary composition is given in Table 2.

Table 2: Exemplary composition of a grinding slurry according to [4]

Element (in wt.-%)							
Nd	Fe	B	Dy	Pr	Al	C	O
19,5	Bal.	0,8	2,4	4,9	0,2	1,3	5,6

The amount of oxygen and carbon is much higher than in the machined magnet. Carbon can be introduced to the system because of the abrasion of the grinding media but mostly because of the organic cooling agent, whereas oxygen is also inserted from the ambient air since temperatures of up to 1000 °C [5] occur during grinding. The different amounts vary strongly depending on composition and the physical treatment before pyrolysis.

1.3 Recycling of NdFeB magnet material

Due to volatile matters and the adverse influence on their vaporization within the pyrometallurgical process, the remaining amount of cooling agent is considered to be the main impurity hindering a direct remelting of the metallic swarfs. In addition, the grinding swarfs as single particles tend to form agglomerates due to their particle shape. These agglomerates incorporate parts of the remaining cooling agent.

The main requirements for an optimal pre-treatment process deriving from the composition and the material properties of the grinding slurries are to minimize the amount of organic and volatile substances contained in the cooling agent and to break down the existing agglomerates in order to separate the particles and gain access to the incorporated cooling agent.

According to these requirements, a thermal treatment via pyrolysis fits to the scope of a pre-treatment prior to pyrometallurgical treatment. Pyrolysis is an endothermic process in which organic material is thermally decomposed under anaerobic conditions. In consequence of the rise of temperature during the process caused by continuous external supply of energy, evaporation processes and thus drying of the material occur first. After drying, the degassing phase and chemical decomposition processes take place. They are divided into the phase of charring and the phase of gas formation. [6]

Depending on the educt and the temperature of the pyrolysis, the following products are formed:

- coke,
- tars, oils, condensable hydrocarbons,
- water released by decomposition (the aqueous condensate) and
- non-condensable pyrolysis gases [6]

Together with the remaining inert material, the coke forms the solid residue. In the condensate tars, oils, condensable hydrocarbons and the water released by decomposition remain. The remainder escapes as pyrolysis gas. [6] The temperature of the pyrolysis process, the residence time in the pyrolysis furnace and the heating velocity of the educts determine the proportions of the pyrolysis products. The pyrolysis process aims to concentrate the metallic swarfs in the solid residue while volatile components end up either in the liquid condensate or in the gas phase. Carbon remaining in the solid phase is been solidified.

After the product has been pyrolysed, a separation of the iron from the rare earth elements is desired. This has already been investigated by Nakamoto et al. [7] for non-pyrolysed grinding slurries. The separation into a metallic phase of iron and a rare earth oxide phase is supposed to take place due to the very different oxygen affinity of the elements. The phase diagrams of the systems Fe-Nd-O at 1077 °C, Fe-Dy-O at 977 °C and the system Fe-Pr-O at 1027 °C are shown in the following Figure 2.[7]

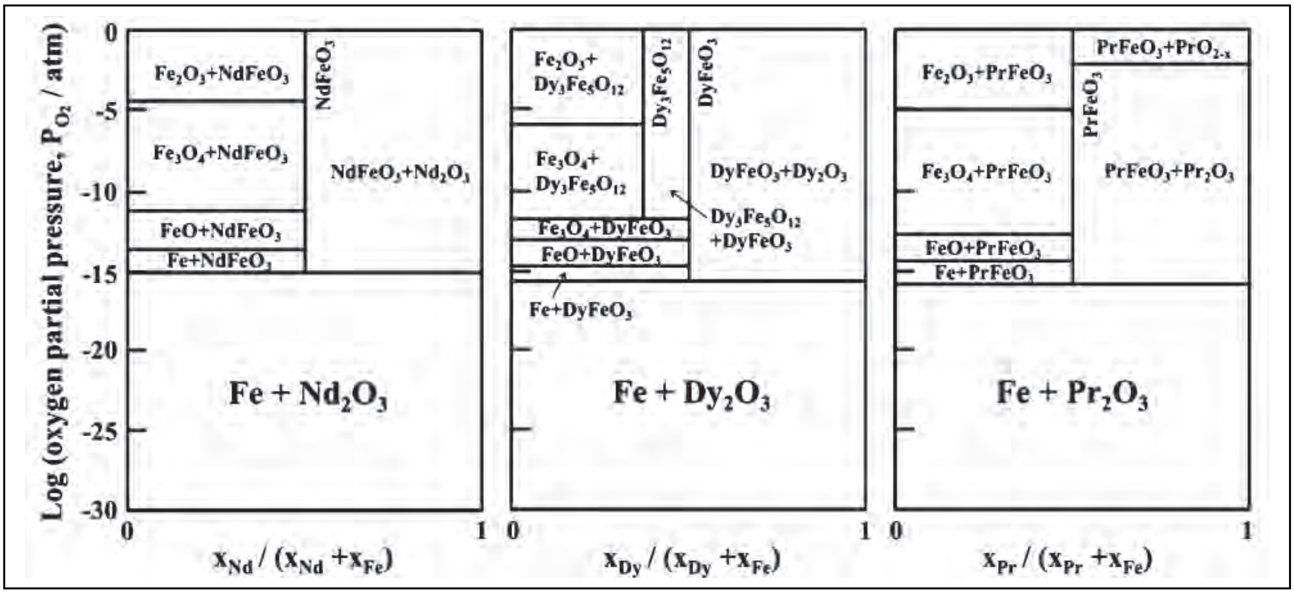

Figure 2: Phase diagrams of the systems Nd-Fe-O, Dy-Fe-O and Pr-Fe-O [7]

In the graphs, the oxygen partial pressure is shown above the respective proportion of rare earths. It is to recognize, that the two phases are present at a low partial pressure of oxygen in the form of iron and rare-earth oxide regardless of the rare earth content. Up to a mole fraction of 0.5 iron oxides and REFeO compounds are formed at higher oxygen partial pressures. From a REE content of 0.5 REO and REFeO are formed. With this diagram, no statement can be made about the separation of the phases and the existence of the phases in the border areas. To work within the range of the desired oxygen partial pressure, in which iron and REO exist separately from each other, a carbon crucible is used. According to the Ellingham diagram, carbon is suitable to reduce iron oxide to iron, while rare-earth oxides cannot be reduced at the experimental temperatures. In addition, a growing ratio of carbon in the iron decreases the melting point of the alloy.

After washing, the material was heated under argon atmosphere at various temperatures, kept there for a certain time and subsequently cooled. In addition, the influence of adding carbon at different temperatures and holding times has been examined. At 1550 °C holding times of 1 to 16 hours were adjusted. According to Nakamoto et al.[7], holding time influences the phase separation between slag and metal. While for a holding time of 1 h the phases appear separately side by side, the oxide phase covers the metal phase with increasing holding time. The iron content in the metal phase hardly changes by extending the holding time. The contents of rare earth elements and cobalt are also not affected. The boron content of the slag phase decreases with the holding time while the content in the metal phase increases. This can be explained by a reduction of the boron oxide with carbon present.

2 Experimental work

The experimental part is divided into two different sections, the first one being the pyrolysis, which is necessary to reduce the remaining amount of organic material in the grinding slurries after solid/liquid separation and to avoid agglomeration. The second step comprises melting of the material with phase separation into a metallic iron phase and an oxide phase containing the rare earth elements taking place shortly afterwards.

2.1 Pyrolysis

The experiments for the thermal minimization of the remaining cooling agent and the disintegration of existing agglomerates were carried out in a pilot-plant scale batch pyrolysis reactor.

Within framework tests different pyrolysis temperatures as well as different retention times were investigated. The temperatures were varied between 200 °C and 650 °C. The retention time was reduced in iterative steps from 60 minutes down to 15 minutes.

For each test a batch of 0.5 kg grinding slurries is filled into the batch reactor. Afterwards, the reactor is closed and placed in the pyrolysis furnace. The batch reactor is connected to the condensate tanks via exhaust pipes for the generated pyrolysis gases. Since the pyrolysis takes place under anaerobic conditions, the batch reactor is purged with argon for five minutes before heating. In order to measure the effective temperature in the reactor, it is equipped with three thermocouples, which allow the monitoring of the temperature in the center of the reactor and on its inner and outer wall.

The gases generated within the process are passed through the condensate tank where a portion of the gases is condensed due to the water cooling. It remains in the condensate tanks as liquid phase (condensate). The remaining, non-condensable gases pass further to a burner where the gases are burned with a flare before they enter an extractor hood. After reaching the aimed pyrolysis temperature and holding it for the aimed retention time, the furnace is turned off and the solid remainder is completely cooled down. Subsequently, the pyrolysed material and the resulting condensate can be removed and recorded.

A retention time of 15 minutes and a pyrolysis temperature of 600 °C were experimentally identified as optimal process parameters in order to minimize the amount of cooling agent. Microscopical analyses of the pyrolysis educts and products prove the disintegration of existing agglomerates, which is shown in Figure 3.

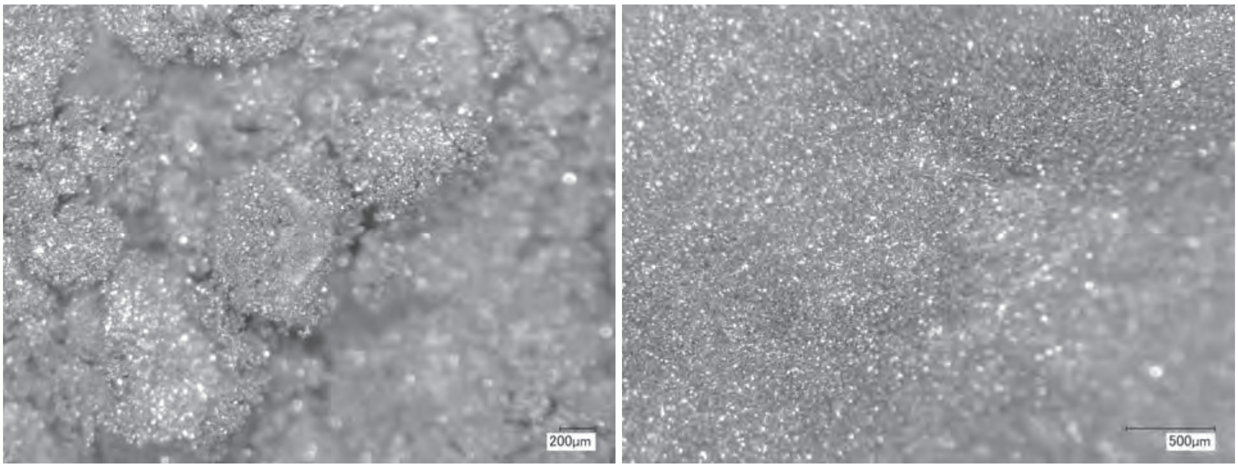

Figure 3: Microscopic pictures of the educt (left) and product (right) of the pyrolysis

At a temperature of 600 °C the carbon remaining in the solid remainder of the pyrolysis is transformed into a solidified coke. The comparison of the chemical composure of educts and products shows that a part of the carbon previously found in the liquid cooling agent was transferred into the solid phase. For further pyrometallurgical processing, the percentages of carbon and oxygen in the solid remainder are relevant. The evaluation of the experiments leads to the conclusion that storage and amount of remaining cooling agent or moisture influence the percentages of oxygen and carbon in the solid pyrolysis product which is further treated for recycling.

2.2 Selective Oxidation

The process of selectively oxidizing the pyrolysed material is performed due to the highly negative oxidation potential of REE. The process aims to create an oxide phase which is rich in REE and a metal phase containing the iron, cobalt and other accompanying elements. The losses of the elements in the opposite phase should be as low as possible.

The amount of oxygen contained in the grinding slurries is high enough to oxidize not only the sum of REE but also aluminium, boron and a part of the iron. The actual structure of the slurries after pyrolysis cannot be clarified completely, but it is expected that different kinds of mixed oxides are formed not only during pyrolysis but most of all during the grinding itself.

For the experiments, carbon crucibles are used due to their suitability as susceptor in an induction furnace and their estimated lack of interdependency with the created slag phase. Nevertheless, carbon reacts with the formed iron metallic phase resulting in a carbon rich cast iron. The general setup of the trials is demonstrated in Figure 5.

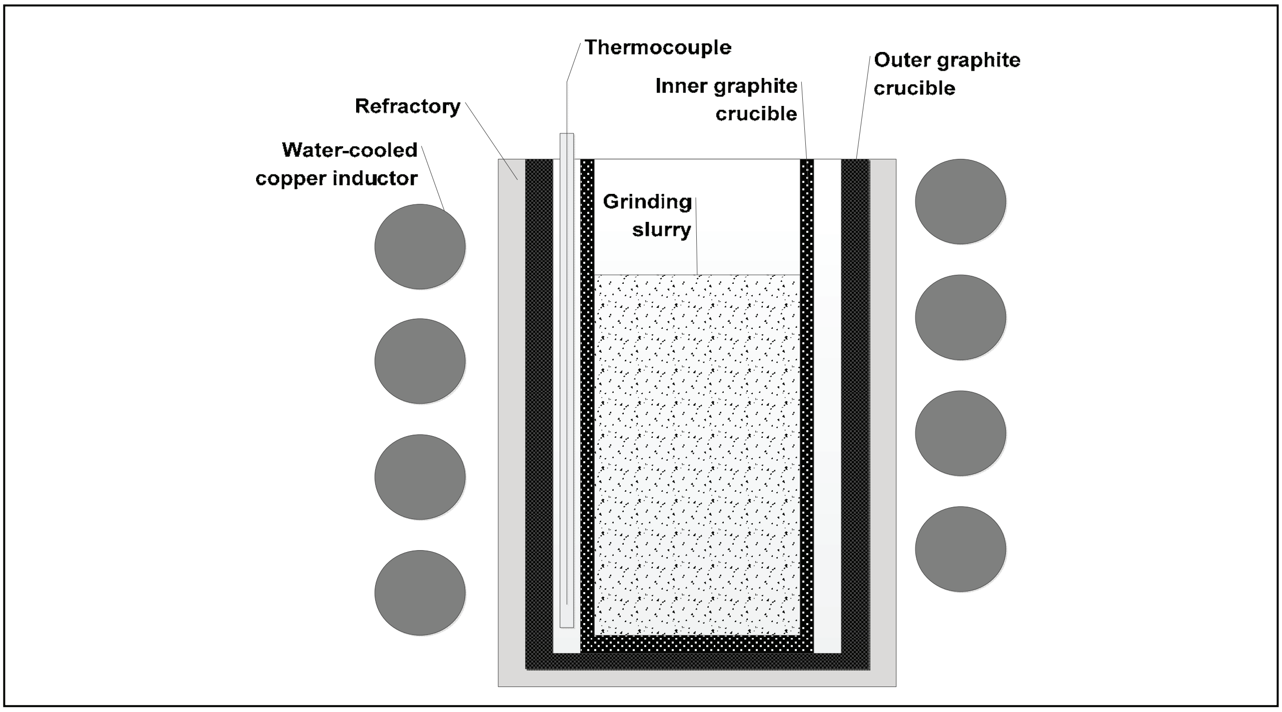

Figure 4: Setup of the melting trials

The graphite crucible is placed centrally in the water-cooled copper coil and is enclosed by a second graphite crucible, which serves as a susceptor. Between the crucibles, a thermocouple is set to track the approximate temperature development. At high temperatures, the measured temperature between the crucibles corresponds well with the actual temperature in the material. Because of the low bulk density of the starting material, relatively little material can be inserted. The two crucibles are isolated by insulating mat to prevent heat dissipation.

At the beginning of the experiment, the furnace is repeatedly evacuated and then flooded with argon to 750 mbar before starting the heating process. First evaporation phenomena are observed in the low temperature range of 400 - 500 °C. This is believed to be a residue from pyrolysis. However, the smoke generation is comparatively low. The melting point of the grinding slurries cannot be uniquely determined due to the inhomogeneity of the material and therefore must be held optically through a sight glass. Melting is preceded by a sintering process, which results in a significant shrinkage of the grinding slurry. After melting a noticeable bubbling is observed, which can be explained by escaping oxygen or CO/CO_2. At best phase segregation is evident subsequent to the fading of gas emissions. Here, the slag phase is formed above the molten metal phase and solidifies. The end of the experiment is characterized by a lack of agitation in the melt.

The phase separation after the end of the experiment can be seen on the left of Figure 5. Due to the small amount of starting material, the slag phase has not settled above the metal phase but sideways. The slag phase has a characteristic blueish colour indicating the presence of rare earth oxides. The graphite crucible is greatly affected by the metal phase, which is why the mechanical separation of the metal from the crucible is difficult.

However, this trend is not evident in all experiments performed. The melting is not possible in every experiment. In all cases, shrinkage is seen but material sometimes cannot or can only be partially melted. This manifests itself in an agglomerate with melt droplets as well as sintered starting material. Phase separation is not recognizable. Both phenomena can be seen in Figure 5.

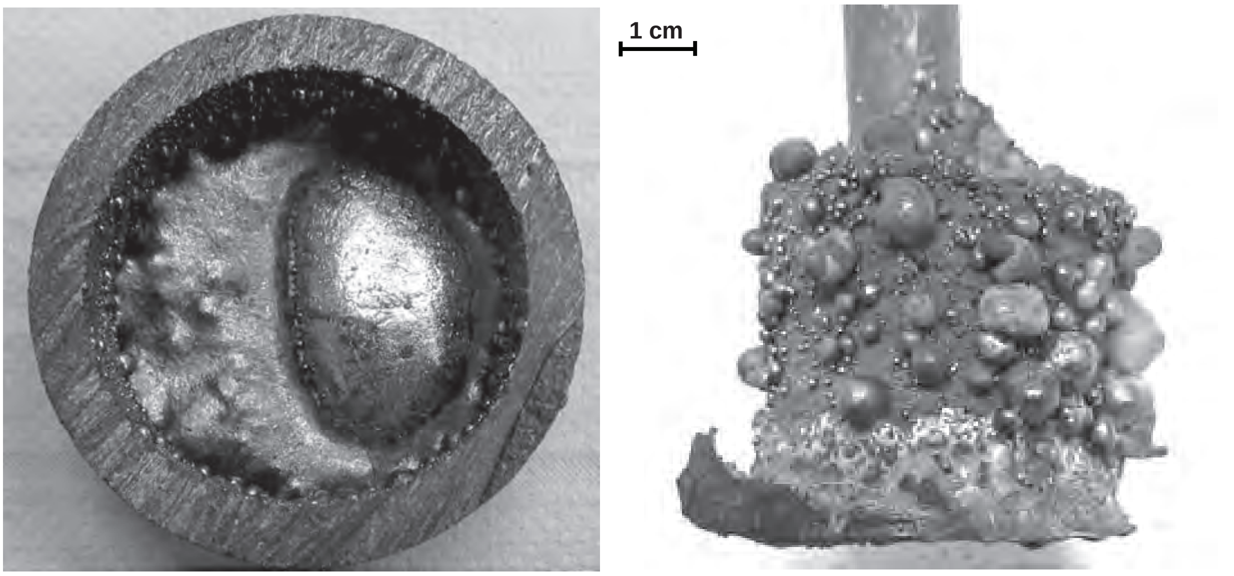

Figure 5: Separated phases after melting (left) and agglomeration with melt droplets (right)

Considering the mass balance, it appears that upon successful phase separation, the slag phase accounts for about 30 % and the metal phase for 60 - 65 % of the input. There is a difference of 5 - 10 % in the form of various losses. This is shown in the following Figure 6.

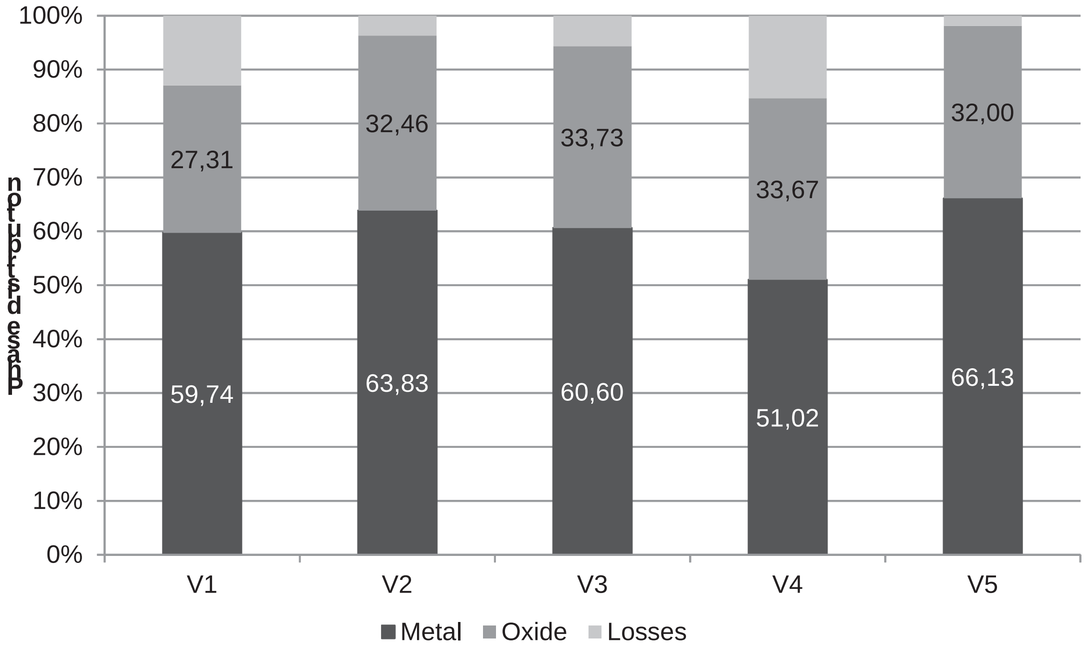

Figure 6: Phase distribution in relation to the input material

In total, the analyses of the single phases show a good separability of iron and rare earth elements. The content of the elements in the non-target phase can be reduced to less than 0.5 wt-%. It can be assumed that the metal phase consists to more than 90 wt.-% of iron and the formed rare earth oxides are contained to more than 90 wt.-% in the slag phase. Most likely, the rare earth elements are available in the form of RE_2O_3, but also formation of mixed oxides is possible. In addition to the rare earth elements, some aluminum and boron is present in the slag phase. Since no longer holding times than 15 min have been adjusted, a lowering of the boron content in the slag phase as mentioned in [7] could not be achieved. The main accompanying elements in the metal phase are cobalt and carbon which can account up to 5 wt.-% each.

Considering the analysis of the input material, it is striking that the most significant difference between meltable and non-meltable slurries can be found in the oxygen and carbon content. Here, a high content of oxygen seems to favour the melting operation, which has to be revealed in further experiments.

3 Conclusions

In summary, it can be said that a phase separation is possible by melting the grinding slurries, which have been successfully pyrolysed under certain conditions. Here, the contents in the complementary phases can be reduced severely. However, this is not feasible with each input material, which can be explained by the influence of oxygen and carbon contained in the material. Below a certain limit, melting can only be achieved partially; a phase separation is hereby excluded. Further studies have to be carried out to show which oxygen and carbon content is necessary in order to realize the melting.

The possibility of a pyrometallurgical separation of an REE-enriched phase after thermal pre-treatment has been proven in small size and pilot-plant scale experiments. An upscaling of these experiments will be investigated. Furthermore, pre-conditioning methods like compaction and the influence of storage should be evaluated in experiments.

In order to assess the economic feasibility of the recycling process, a subsequent hydrometallurgical treatment must be taken into consideration as saleable concentrates with high purities are required. An assessment of the saleability of the concentrates after each processing step is necessary.

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