

RARE EARTHS: ESSENTIAL ELEMENTS FOR THE TRANSITION TO A LOW-CARBON ECONOMY

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Abstract

This paper gives an overview of rare earths in three main applications that are essential for a sustainable use of energy resources: (1) permanent magnets; (2) nickel metal hydride batteries and (3) lamp phosphors. Strong neodymium-iron-boron magnets are used in electric and hybrid electric cars, in electric bicycles and in wind turbines. Nickel metal hydride batteries are together with lithium-ion batteries the obvious choice for storing electric energy in electric and hybrid electric cars. Lamp phosphors are used in fluorescent lamps, compact fluorescent lamps (CFLs) and in light-emitting diodes (LEDs), which are all more energy-efficient forms of lighting than the old-fashioned incandescent lamps. For these applications, the following rare earths are of importance: neodymium, europium, terbium, dysprosium and yttrium.

Introduction

The rare earths or rare-earth elements (REEs) are a group of 17 elements in the periodic system, including neodymium (Nd), europium (Eu), terbium (Tb), dysprosium (Dy) and yttrium (Y). The rare earths are becoming increasingly important because they are so-called “product enablers” that give unique properties to advanced materials and that play a key role in the performance of high-tech materials. Rare earths are essential for permanent magnets, nickel metal hydride batteries and lamp phosphors.^{1,2} The increasing popularity of hybrid and electric cars, electric bicycles, wind turbines and compact fluorescent lamps has caused an unprecedented increase in the demand and rare earths since 2004. In fact, the green economy cannot further develop without rare earths.^{3,4} This paper gives an overview of the use of rare earths in the three main energy-related applications of rare earths: (1) permanent magnets; (2) nickel metal hydride batteries and (3) lamp phosphors. These three applications represent about 35% of the consumption of rare earths by volume: magnets (20%), batteries (8%), phosphors (7%), on a yearly total consumption of about 120,000 tonnes of rare-earth oxides. However, these three applications represent no less than 75 % of the rare-earth market by value.

Permanent magnets

Permanent magnets are the most important application of rare earths, both according to consumed volume of rare earth oxides and according to consumption measured by value. Moreover, rare-earth permanent magnets are a fast growing market. The magnetic field produced by rare-earth permanent magnets can be in excess of 1.4 Tesla, whereas that of the older ferrite and ceramic magnets is only between 0.5 and 1.0 Tesla. There are two main types of rare earth magnets: samarium-cobalt magnets and neodymium-iron-boron magnets.⁵ The present market is dominated by neodymium-iron boron magnets (>95 %).

Samarium-cobalt magnets were the first class of rare earth magnets invented, and were developed in the 1970s.⁶ Typical compositions of the samarium-cobalt alloys are SmCo_5 and $\text{Sm}_2\text{Co}_{17}$. They are less used than the neodymium-iron-boron magnets because of their higher costs and weaker magnetic field strength. However, samarium-cobalt alloys have higher Curie temperatures, creating a niche for these magnets in applications where a high magnetic field strength is needed at high operating temperatures. The maximum use temperatures range between 250 and 550 °C, whereas the Curie temperatures are between 700 to 800 °C. They are highly resistant to oxidation, but sintered samarium-cobalt magnets are brittle and prone to chipping and cracking and may fracture when subjected to thermal shocks. The samarium-cobalt magnets are good resistant against demagnetisation. SmCo_5 has a maximum energy product $(\text{BH})_{\text{max}}$ of 130 to 200 kJ/m^3 , whereas that of $\text{Sm}_2\text{Co}_{17}$ is from 160 to 260 kJ/m^3 . The size of the samarium-cobalt magnet industry worldwide is approximately 1000 tonnes of alloys. The samarium-cobalt magnets are expensive and subject to price fluctuations, because cobalt is market price sensitive.

Neodymium-iron-boron magnets (NdFeB magnets) invented in the 1980s by General Motors Corporation and Sumitomo Special Metals, are the strongest known types of permanent magnets.⁷ A NdFeB magnet can lift 1300 times its own mass. By volume one requires about 18 times as much ceramic magnet material for the equivalent magnet strength. The composition of the magnetic alloy is $\text{Nd}_2\text{Fe}_{14}\text{B}$. The NdFeB alloy has a maximum energy product $(\text{BH})_{\text{max}}$ of 512 kJ/m^3 . Although NdFeB magnets have stronger magnetic field strength, they are inferior to samarium-cobalt magnets in resistance to oxidation and Curie temperature. Use of protective surface treatments such as nickel, zinc, tin or gold plating or epoxy resin coating can provide corrosion protection where required. The NdFeB magnets will begin to lose magnetic strength if they are heated above their maximum operating temperature, which is 80 °C for standard NdFeB alloys. They will completely lose their magnetisation if heated above their Curie temperature, which is 310 °C for standard NdFeB alloys. NdFeB alloyed with up to 4 wt% dysprosium can dramatically increase the maximum operational

temperature. These modified alloys can be used to temperatures up to 200 °C. The drawback of dysprosium addition is that the maximum field strength of the magnet is decreased. If supply were no object, terbium would probably be the additive of choice, as it has a stronger influence on coercivity (a measure of the resistance of a ferromagnetic material to becoming demagnetised) with a lesser impact on remanence (magnetisation left after an external magnetic field is removed). NdFeB magnets are much less brittle than samarium-cobalt magnets. Even with this improved mechanical strength they should not be considered as structural components, and have to be handled with some care to minimise any possible chipping or breakage.

The two principal manufacturing routes for NdFeB magnets are: (1) classical powder metallurgy or sintered magnet process; (2) the rapid solidification or bonded magnet process. *Sintered magnets* are prepared by pulverising an ingot precursor to microcrystalline size, followed by sintering the magnetically aligned powder into dense blocks which are then heat-treated, cut to shape, surface-treated and magnetised. Currently, around 70,000 tonnes of sintered neodymium magnets are produced each year, mainly in China and Japan. *Bonded magnets* are prepared by melt-spinning a thin ribbon of the NdFeB alloy. The ribbon contains randomly oriented Nd₂Fe₁₄B nano-scale grains. This ribbon is then pulverised into particles, mixed with a polymer and either compression or injection molded into bonded magnets. Bonded magnets offer less flux than sintered magnets but can be formed into intricately shaped parts and do not suffer significant eddy current losses. There are approximately 10,000 tonnes of bonded NdFeB magnets produced each year.

NdFeB magnets are typically used in most computer hard disk drives, in mobile phones and in a variety of audio applications such as loudspeakers and headphones. Their greater strength allows smaller and lighter magnets to be used for a given application. This is particularly useful for mobile phones, and particularly in the automotive and wind power industries. Electric motors made with NdFeB magnets are about half the weight of traditional ferrite motors, and have found many applications in electric seats, windows and mirrors, in the starter motor and alternator, whilst replacing hydraulic systems for steering. NdFeB magnets reduce weight of the car and reduce power consumption.

Hybrid electric vehicles (HEVs), plug-in hybrids (PHEVs) and pure electric (EVs) all require an electric motor. At present the vast preponderance of HEVs use a Permanent Magnet Brushless Direct Current (PMDC) motor and this contains NdFeB magnets. The best performing magnet is a sintered magnet of composition Nd-31 %-Dy-4.5 %-Co-2 %-Fe-61.5 %-B-1 % (wt%). Dysprosium is critical in this application to give resistance to demagnetisation at high temperatures as the magnet reaches

service temperatures of 160 °C. A motor can be up to 100 kW, although 55 kW is a reasonable figure. For a 55 kW motor 0.65 kg of Nd-Dy-Co-Fe-B alloy is required, which gives 200 g of neodymium per motor (3.6g/kW) and 30 g of dysprosium per motor (0.55g/kW). A 25 kW generator is typically required to recoup braking energy so for analysis purposes a hybrid vehicle contains 288 g of neodymium and 44 g of dysprosium.

A gearbox wind turbine contains 80 to 100 kg of NdFeB magnets per MW, which is equivalent to 20 to 35 kg of pure neodymium per MW. Direct drive wind turbines contain 700 to 1200 kg of NdFeB magnets per MW, which corresponds to 175 to 420 kg of pure neodymium per MW. Other types of wind turbines contain less or even no neodymium. The vast majority of commercial wind turbines use gearboxes. Permanent magnet direct drive turbines only make up a small portion of the total wind turbines sold. In contrast to NdFeB magnets used in electric cars, NdFeB magnets for wind turbines do not require addition of dysprosium. Dysprosium is used in magnets for operating at higher temperatures, an environment that is not likely to be present in a well-designed wind turbine. Moreover, there is wind that can be used to keep the magnet cool.

A new and growing market for NdFeB magnets are the electric bicycles. These electric bicycles contain lightweight, compact, NdFeB magnets for their miniature motors. They use approximately 350 g of NdFeB per electric bicycle, or 86 g of neodymium per electric bicycle. There does not appear to be an alternative to NdFeB in bicycles due to space and weight considerations.

Hydrogen storage and battery alloys

The use of rare-earth alloys in rechargeable *nickel metal hydride (NiMH) batteries* is based on their hydrogen-storage properties.⁸⁻¹⁰ LaNi₅ as a representative of hydrogen storage materials is capable of absorbing considerable amounts of hydrogen gas and is forming a hydride LaNiH₆. The hydrogen density in LaNiH₆ is even higher than that of liquid hydrogen. A cubic meter of LaNiH₆ can contain 88 kg of hydrogen, but the same volume of liquid hydrogen only weights 71 kg. The LaNi₅-related hydrogen storage alloys absorb hydrogen gas rapidly at ambient temperature and their hydrides can easily be dehydrided by heating. The following hydriding and dehydriding reactions can take place repeatedly:



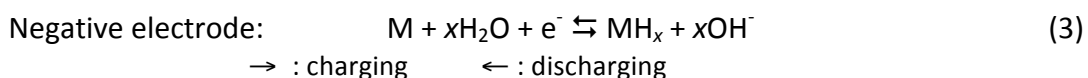
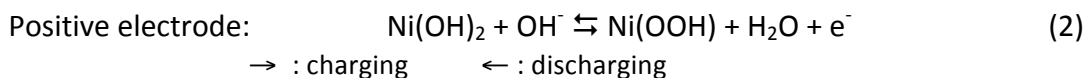
The rare earth hydrogen storage alloys are ideal materials for hydrogen storage because their absorption and desorption cycles can be realised at moderate

temperatures and pressures. The intermetallic compound LaNi_5 crystallises in the CaCu_5 -type hexagonal structure. During the hydride formation reaction, the hydrogen atoms enter into the LaNi_5 lattice, resulting in a severe deformation, but the symmetry of the hexagonal crystal structure remains unchanged. The lattice expansion of the LaNi_5 compound is 23.4 % upon hydriding to LaNi_5H_6 . At low hydrogen pressures, the formation of metal hydride strongly depends on the hydrogen pressure. However, as soon as the hydrogen pressure increases above a certain pressure, the plateau pressure, the quantity of hydrogen absorbed is nearly independent of the pressure. In the plateau region, LaNi_5 is completely transformed into LaNi_5H_6 . The hydride is decomposed if the hydrogen pressure decreases or upon heating of the hydride.

LaNi_5 -based alloys are ideal hydrogen storage alloys, but their prices are high because pure lanthanum should be used as raw material. In order to reduce the price of the alloy, mischmetal (Mm) is used to replace pure lanthanum, forming a family of mischmetal- Ni_5 based hydrogen storage alloys.

Mischmetal is a mixture of light rare earth elements (La, Ce, Pr, Nd) in the metallic state. The composition of mischmetal varies depending on the origin of the rare-earth minerals and its processing. Its composition affects the characteristics of the hydrogen storage alloys. The higher the content of cerium and neodymium in mischmetal, the higher the dissociation pressure of the hydride will be. The plateau pressure of MmNi_5 alloys is much higher than that of LaNi_5 . To reduce the plateau pressure of MmNi_5 alloy, Ni should be substituted by other elements. Usually Al, Mn, Cr, Fe, Co Cu and Si are used as the third constituting element, and Ti or Zr as the fourth element. The effectiveness of these elements on the plateau pressure is $\text{Mn} > \text{Al} > \text{Cr} > \text{Si} > \text{Fe} > \text{Co} > \text{Cu}$. A series of MmNi_5 based alloys such as $\text{MmNi}_{4.5}\text{Mn}_{0.5}$, $\text{MmNi}_{4.5}\text{Mn}_{0.45}\text{Zr}_{0.05}$, $\text{MmNi}_{4.5}\text{Al}_{0.5}$, $\text{MmNi}_{4.5}\text{Al}_{0.45}\text{Ti}_{0.05}$, $\text{MmNi}_{4.5}\text{Cr}_{0.5}$, $\text{MmNi}_{2.5}\text{Co}_{2.5}$ have been developed. The plateau pressure for hydride formation should not be too high for safety reasons. Plateau pressures of 1 to 5 atm, at temperatures ranging from 0 to 50 °C are suitable for the purpose of hydrogen storage.

In the *nickel metal hydride (NiMH) battery*, the negative electrode is made of a hydrogen storage alloy, replacing the cadmium in the older Ni-Cd rechargeable battery. During charging and discharging of a NiMH battery, the following electrode reactions occur:



where M and MH are the hydrogen storage alloy and its corresponding hydride. The overall reaction of a NiMH battery is:



→ : charging ← : discharging

The NiMH battery has the same cell potential as the Ni-Cd battery (1.2 V), but it offers several advantages. These include a capacity that is 1.5 times higher than that of a standard Ni-Cd battery. The battery has no memory effect, fast charging and discharging is possible. They have a good performance at lower temperatures. Because the toxic cadmium is absent, they are environmentally friendlier. Two types of hydrogen storage alloys are being used in NiMH batteries: AB₂ Laves phase alloys and AB₅ type alloys of which LaNi₅ is a typical representative.

Hybrid electric cars represent more than half of the usage of NiMH batteries. The battery stores energy normally wasted during coasting and braking and saves it until needed by the electric motor. There is currently a great deal of debate surrounding the relative advantages and disadvantages of NiMH batteries compared to lithium-ion (Li-ion) batteries. Toyota is using NiMH batteries in its Prius, but other manufacturers, such as Renault, plan to use Li-ion batteries in their forthcoming electric cars. Every Toyota Prius contains 10 to 15 kg of lanthanum in its battery pack. Deutsche Bank forecast that the market share of Li-ion batteries will be rising to 70 % of the hybrid market between 2015 and 2020. However, if the tendency to shift from NiMH to Li-ion batteries for powering electric and hybrid cars will continue, there will be an oversupply of lanthanum on the market.

Lamp phosphors

Rare-earth lamp phosphors are found as a layer on inside of the glass wall of fluorescent lamps or compact fluorescent lamps (saving lamps). The lamp phosphors convert the ultraviolet emission of a noble-gas/mercury discharge plasma into visible (white) light. The phosphors are responsible for nearly all the visible light produced by the lamp, because the visible mercury lines are contributing only a few percent to the total lamp light output. White light can be generated in different ways. The simplest one is to mix blue and orange. It is also possible to mix blue, green and red. The combination of a number of emission bands to a continuous spectrum also yields white light. From the mid-1970s, blends of three rare-earth activated phosphors, known as *tricolor* or *triphosphor* blends, replaced the older phosphors.¹¹ Most blends consist of Y₂O₃:Eu³⁺ (red emitting phosphor), LaPO₄:Ce³⁺, Tb³⁺ (green emitting

phosphor) and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (blue emitting phosphor). The contribution of the red phosphor to the blend is the largest (~ 60 wt%), followed by the green component (~ 30 wt%). The amount of the blue component is only about 10 wt%, because the atomic emission spectrum of mercury can provide some blue lines.

The emission spectrum of the red-emitting $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor consists of a dominant peak around 611 nm. The commercial formulations contain relatively high europium concentrations (3–5 mole percent). At lower Eu^{3+} concentrations emission, also emission in the the green-yellow occurs, at the expense of the red emission. The $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor absorbs the 254 nm mercury discharge emission through a charge transfer transition involving the Eu^{3+} ion and the neighboring O^{2-} ions. This charge transfer transition peaks at about 230 nm. Hence, the absorption of 254 nm radiation is not very high, and about 25 percent of this radiation is reflected by the phosphor due to its high reflectivity. The reflectivity can be decreased with an increase in the europium concentration, but the high cost of europium-based phosphors prohibits such compositions. The high reflectivity and the fact that the green and blue phosphors are stronger absorbers of the 254 nm radiation requires the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor to be the dominant component (by weight) of the triphosphor blend. The quantum efficiency of this phosphor is close to unity and constant in the range of europium concentrations from 1 to 15 mole percent. The quantum efficiency is the highest of all lighting phosphors. High purity Y_2O_3 is required. Impurities in Y_2O_3 tend to act as competing absorbing centers for the 254 nm radiation, but they do not convert it to visible light. One of the most serious impurities is iron. An iron concentration of 5 ppm lowers the quantum efficiency by 7%. The high price of europium and high purity yttrium makes the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor a rather expensive one. Research aimed at replacing this phosphor with less-expensive alternatives have not met with success. The high quantum efficiency, near perfect red emission and exceptional lumen maintenance are the reasons for the application of the $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor in fluorescent lamps for more than three decades.

The first green phosphor in tricolor blends was $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}$. The compound $\text{CeMgAl}_{11}\text{O}_{19}$ is an efficient ultraviolet emitter when excited by 254 nm radiation. The emission arises from allowed transitions between the ground and excited states of the Ce^{3+} ion which are derived from the $4f^1$ and $5d^1$ electronic configurations, respectively. The introduction of Tb^{3+} in $\text{CeMgAl}_{11}\text{O}_{19}$ quenches the Ce^{3+} emission and generates the green Tb^{3+} luminescence as a result of the Ce^{3+} -to- Tb^{3+} energy transfer. A rather high Tb^{3+} concentration (33 mole percent) is required for the complete quenching of the Ce^{3+} emission. The optimum phosphor composition $(\text{Ce}_{0.67}\text{Tb}_{0.33})\text{MgAl}_{11}\text{O}_{19}$ exhibits high quantum efficiency and excellent lumen output and maintenance during lamp operation. The phosphor synthesis requires high

temperatures (1500 °C) to promote reaction between rather refractory starting materials. A reducing condition during synthesis is required to maintain cerium and terbium in the trivalent state. The $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ phosphor has largely replaced the $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}^{3+}$ phosphor. The advantages of $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ are the manufacturing ease due to the lower synthesis temperatures (about 1000°C) and the lower terbium concentrations required for optimum performance. The commercial formulation contains 27 % of cerium and 13 % of terbium ($\text{La}_{0.60}\text{Ce}_{0.27}\text{Tb}_{0.13}\text{PO}_4$), and has an emission maximum at 543 nm. A third green phosphor used in fluorescent lamps is $\text{GdMgB}_5\text{O}_{10}:\text{Ce}^{3+},\text{Tb}^{3+}$. The Gd^{3+} ions assist in the transport of energy from the sensitizer (Ce^{3+}) to the activator (Tb^{3+}) ions. Energy transfer from Ce^{3+} to Gd^{3+} energy transfer is an efficient process. Efficient green luminescence is generated when the activator ions (Tb^{3+}) trap the excitation energy that is being transferred from Gd^{3+} ion to Gd^{3+} ion. The quantum efficiency is high and the phosphor displays excellent stability in fluorescent lamps.

The most popular blue-emitting phosphor is Eu^{2+} -activated $\text{BaMgAl}_{10}\text{O}_{17}$ (also called BAM). A second commonly used blue phosphor is Eu^{2+} -activated $(\text{Sr},\text{Ba},\text{Ca})_5(\text{PO}_4)_3\text{Cl}$. The phosphors have an emission band with a maximum at 450 nm, and their quantum efficiency is about 90 %. The blue phosphors represent only a minor weight fraction of the triphosphor blend (about 10 percent for color temperature of 4100 K). However, blends designed for higher color temperatures, say 6500 K, require higher amounts of the blue emitting component.

The development of highly efficient and high-color-rendering fluorescent lamps would not have been possible without the application of rare earth phosphors. Compact fluorescent lamps would not have been possible without the development of rare-earth phosphors, as their higher wall temperature and higher ultraviolet flux quickly degrades halophosphate phosphors. The main disadvantage of the rare-earth phosphors is their high cost which has more than doubled the cost of some fluorescent lamps. As a compromise between phosphor cost and performance a double coating scheme is widely used in the fluorescent lamp industry. In this scheme a relatively light coat of the high performance rare earth phosphor blend is coated over a base layer of inexpensive halophosphate phosphor. The rugged rare-earth phosphor coating is directly exposed to the discharge, generating white light with high efficiency and with a good color rendering index while protecting the more-easily-damaged halophosphate phosphor.

The application of rare-earth phosphors in white LEDs is skyrocketing. Most white light LEDs generate are blue GaN or GaInN LEDs and part of the blue light emitted by the LED is absorbed by a phosphor and re-emitted at a longer wavelength A blue LED and a yellow phosphor generated white light. Ce-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (Ce:YAG) is often

the yellow phosphor of choice. White light can also be generated, albeit less efficiently, by a near-ultraviolet emitting diode in combination with a blue, green and red phosphor.

A growing market for rare earth phosphors are LCD screens. Because an LCD screen does not emit light on its own, it needs backlighting. Although white LEDs can be used, cold cathode fluorescent lamps remain popular for LCD backlighting. Both types of backlighting contain rare earths. As mentioned above, the white LEDs are essentially a blue-emitting diode in combination with the yellow Ce-doped $Y_3Al_5O_{12}$ phosphor. The working principle of the cold cathode fluorescent lamp is very similar as that of conventional fluorescent lamps, with the difference that the former is operating below its thermionic emission temperature. It is possible to use a red, green and blue rare-earth phosphor to convert the ultraviolet radiation into visible light. These phosphors can be the same as in the tricolor phosphor mixture for fluorescent lamps.

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