The Application of Rare Earth Metals Is Widening

Despite Lack of Engineering Data.

By Roman Lundin and John R. Wilson

Abstract

Uses of the pure rare earth metals or of alloys containing them as a dominant component have understandably been limited by their high cost, extreme sensitivity to contaminants, poor mechanical properties, high chemical reactivity and, most significantly, by a broad lack of physical property data and metallurgical information on these materials. Nevertheless, they are finding increasing uses as low-level but very important alloying additives for stainless steels and for aluminum alloys, silicon alloys and magnesium alloys. In addition to their historical use in spark igniters (e.g., lighter flints or ferrocerium rods) and the so-called "supermagnet" alloys such as gadolinium-cobalt, the rare earths are also finding new uses in superconducting devices, lithium/metal hydride batteries and a wide variety of ceramic and other materials. This paper reviews what is known of the physical and chemical characteristics of these unusual materials and discusses many of their current and potential future commercial uses.

1. What are the Rare Earths?

The rare earth elements or lanthanides consist of fourteen elements plus lanthanum. For practical reasons, the list often includes scandium and yttrium for a total of 17, since these two elements are very similar in characteristics to the lanthanides. For ease of discussion and also for convenience in assessing their potential processability and use, the rare earths are best classified into five unofficial 'groups':

Group 1 lanthanides have *low melting points* and *high boiling points* - lanthanum, cerium, praseodymium, neodymium.

Group 2 lanthanides have *high melting points* and *high boiling points* - gadolinium, terbium, yttrium, lutetium.

Group 3 lanthanides have *high melting points*, *mid to low boiling points* and *a high vapor pressure* at the melting point - dysprosium, holmium, erbium and scandium.

Group 4 lanthanides have *low boiling points* - samarium, europium, ytterbium and thulium.

Group 5 lanthanides - this group contains just one element, promethium, which really belongs in Group 1 but is highly radioactive and for that reason has no significant commercial uses.

The grouping of the lanthanides in this way also correlates with their processing characteristics. For example, the group 3 lanthanides are difficult to handle in vacuum-remelting equipment because of their high vapor pressures - they are better refined by a sublimation method. The group 2 and group 3 lanthanides are difficult to contain in metal or ceramic crucibles as liquids at high temperature because of their high melting points. The group 1 lanthanides offer some of the broadest liquid ranges (LR = BP-MP) of any of the elements. Note that the group 4 lanthanides do not have unusually high vapor pressures close to the melting point despite their relatively low boiling temperatures.

Despite the differences that permit this classification, the rare earths are *chemically* more similar than different, a characteristic that has presented major difficulties in their separation and purification.

1.1 The Rare Earths are NOT Rare…….

The name given to the Rare Earth Metals (REs) dates from ancient Greek times but it misleads a lot of would-be users because these elements are *not* rare. For example, cerium, the most widely-used of the rare earth metals, is more abundant in the earth's crust than tin, while yttrium and neodymium are more abundant than lead. Even hard-to-find lutetium is more abundant than mercury or iodine. Difficulties arise from the fact that while the rare earth elements occur very widely, they are usually found in very low concentrations and in the company of other rare earths.

1.2 ....And the Pure Rare Earths may not be very Pure

The relatively high prices of the REs result not from their rarity but from the extreme difficulty of extracting them from their ores and, more significantly, purifying them. The individual RE elements are extremely difficult to separate from one another and have a very high affinity for most of the interstitial elements that are famous for causing problems or modifying properties in other metals - for example, carbon, oxygen, nitrogen, hydrogen, sulfur, silicon and boron. For this reason, obtaining genuinely contaminant-free RE metals or alloys has always been difficult and remains so. However, there is hope that new high-temperature refining technologies may help to overcome this problem.

Many rare earth products offered as "high purity" may have analyses that ignore the other rare earth elements present or alternatively ignore the interstitial elements not removed during refining. It is not unusual to encounter a "four nines" rare earth that contains as much as 10,000 ppm of oxygen - that amounts to 1 wt. % or, more significantly, 8.6 at. % oxygen - enough to form a considerable volume of internal oxide. And, of course, that means that your expensive "4N" or "5N" metal is really only 2N at best and probably highly embrittled by an internal distribution of oxides or other non-metallic compounds!

The effect of these unrecognized impurities can be very serious. For many applications such as alloying, the presence of other rare earth metals may not be very important. For almost all other uses of the rare earth metals, including permanent magnet and high-TC superconductor applications, the presence of interstitials presents a major problem since they can have a substantial effect on most physical and mechanical properties. The internal oxides and nitrides that form as a result of the failure to remove oxygen and nitrogen, as well as other interstitials, during refining, result in severe embrittlement of all RE metals and alloys for which this problem has been documented. Superficial oxidation or nitridation of an RE metal *after* refining may not be so serious provided that the temperature is low enough to prevent inward diffusion of the interstitial element. However, superficial oxidation can sometimes result in severe surface cracking and failure as a result of 'notch effects'.

Hydrogen is the exception to this - it diffuses quite readily, even at room temperature, and results in the formation of brittle internal hydrides, especially in Lanthanum (which reacts quite vigorously with hydrogen to form dark, friable and non-protective hydrides; for this reason, lanthanum is used in nickel-metal hydride batteries).

1.3 High Cost and Lack of Purity has Limited RE Applications

Many possible engineering and "high-tech" applications of the rare earth metals until this decade have been severely limited by these purity-related property shortcomings. Companies like Arris International that supply metals and fabricated rare earth products see great variations in the quality of raw materials and therefore stress their product reliability as the most important asset. They offer consistent end-product purity and therefore performance. Wider use of REs will require both lower-cost methods of refining and purification and the development of many new applications that have been held back by the purity issue.

1.4 Where's the Data?

A major consequence of the difficulty of obtaining certifiably pure samples of the individual rare earth metals is the almost complete lack of reliable metallurgical data for these materials. Unless data such as tensile or flexural strength and modulus, impact strength, diffusion constants and the like are accompanied by a detailed statement of purity, they should be regarded as suspect. While there is a limited amount of reliable physical data such as melting and boiling points, resistivities and critical temperatures on the REs (see Table 1), there is, in our opinion, almost no mechanical property data that can be certified as reliable. Even the compressivity and elastic modulus data included in Table 1 should be regarded as suspect because both are somewhat affected by impurities in the metal.

1.5 A Major Need for Data-Gathering

The measurement of mechanical property data may no longer be fashionable, especially when it is coupled with the need for extreme-purity materials, but there is a very serious need for better documentation of the RE metals. At present, there is very little basis for judging the potential of using the RE metals for any applications beyond those already well known and which in general do not depend on the mechanical properties of these materials. Certain of the rare earth metals (primarily the group 2 rare earth metals referred to in section 1) offer some interesting combinations of high melting point (1,663 deg. C in the case of lutetium) and low compressibility, suggesting mechanical properties that might fall in the same range as those of lower-density magnesium or aluminum (whose data are included in Table 1 for comparison) but extending to much higher temperature. It hardly seems likely that pure lutetium will have the "soft, can be cut with a knife" consistency reported for cerium and lanthanum, for example, but no reliable data exist to support even this qualitative guess.

1.6 Environmental Interactions; Corrosion

Another problem that severely limits any application of the rare earth metals is the ease with which many of them oxidize, especially in moist air. The oxides that form in air are not usually protective (unlike the cases of aluminum and magnesium) and the metals react quickly, especially at elevated temperature. Small particles of europium, cerium and lanthanum are pyrophoric and the bulk metals slowly convert to a pile of (hydrated?) oxide in air with accompanying contamination of the remaining metal with hydrogen. The corrosion process in the presence of water results in diffusion of hydrogen into the metal with consequent embrittlement. A major challenge to any future use of the rare earths will be to develop a means of protecting the surfaces in use. The higher melting point rare earths may not be as reactive but, once again, the lack of data means that this is impossible to confirm.

2. Established Rare Earth Metallurgical Uses

Rare earths have experienced gradual growth in commercial use since their discovery. Misch metal (generally referred to as Mm), a relatively impure alloy of cerium and lanthanum with other rare earth elements that is the direct result of refining RE mineral concentrates without separation of the individual elements, has been used as a flint material in lighters and firearms for many years. Both cerium and lanthanum are pyrophoric and, as a result, small particles of the alloy ignite in air when struck off the flint. Fortunately, the mischmetal usually contains a high level of both iron and interstitial elements, which make it brittle and easily able to form sparks. Mischmetal has other uses, too. Interstitial and iron-free Mm is being evaluated by a number of researchers as a lower-cost substitute for pure rare earth metals in applications where the presence of other rare earths is non-critical. The problems in applying mischmetal, however, derive from the characteristics that make it effective in flints - the material is typically embrittled by a high interstitial content and by about 5-10 wt % iron (the latter forms numerous intermetallic compounds with the rare earth metals). In addition, mischmetal varies widely in composition according to source; it may be cerium-rich, lanthanum-rich and may contain more or less of Nd, Pr, Sm and several other rare earths. Historically, no attempt has been made to remove the interstitials from mischmetal, which may contain several wt % of these impurities.

2.1 Improving the properties of irons and steels

Rare earth elements, most notably cerium and mischmetal, have also been used as minor alloying additives for controlling inclusions in cast irons and steels. The cerium appears to combine with the sulfide inclusions that are invariably present in these materials to form particles with a more rounded morphology that is less likely to promote cracking. The normal flake-like morphology of graphite particles in nodular irons may also be modified to a spheroidal form that promotes greater ductility. Both results may be due partly to the effect of Ce in modifying the surface properties of the metal or sulfide. The extreme chemical affinity of the rare earth elements for almost anything that they may contact suggests that they will also interact strongly with inclusions in most metals, but little is known about the mechanism by which this occurs.

A more recent discovery suggests that small additions of the lanthanides may confer even greater protection on those metals and alloys that are already well protected from corrosion by oxide films. These include the iron-chromium and iron-chromium-nickel stainless steels (i.e., both the ferritic and austenitic alloys), and most other alloys that are dependent on chromium for their corrosion/oxidation resistance. Further study may suggest that the effect is even broader - e.g., that the protection provided by all spinel-forming oxides such as Al2O3 or Cr2O3 is enhanced in this way. Use of rare earths as alloying additions for corrosion control shows promise of becoming a major growth market.

There is also strong evidence that at least cerium acts as a grain-refining agent in some steel compositions, just as it apparently does for aluminum and magnesium alloys (see below), with corresponding improvements in mechanical properties and fatigue resistance.

2.2 Improving the properties of Non-Ferrous Metals and Alloys

High-Strength Aluminum Alloys

Lanthanide additions have been very effective in enhancing the mechanical properties (UTS, impact) and reducing the notch-sensitivity and increasing the fatigue life of a range of high-strength aluminum alloys, most notably the Al-Li alloys most commonly used for airframe construction. Good results have also been obtained for Al-Fe-V-Si alloys and more recently for the high-silicon Al-Si alloys used for (e.g.) cylinder liners. Corrosion resistance and hence resistance to stress-corrosion cracking is also greatly improved. Cerium or mischmetal are the most commonly-used additives (the amounts required are small, typically much less than 1 wt.%). The mechanism by which the lanthanides achieve this effect is not completely clear. Grain refinement is evident and it appears likely that the morphology of many of the intermetallics present is shifted from platelike toward spherical in shape, which reduces their impact as crack initiators. The effect on the corrosion resistance of these alloys is likely to be due to the effect of cerium (or other lanthanide) oxide on the protective capabilities of Al2O3, but this has not yet been shown, nor has the mechanism been studied.

Much of the recent work on the metallurgical uses of the lanthanides has been reported from China, a country that is a major rare earth metal producer, but work in Europe and in the U.S. has begun to confirm these findings. We have no reason to suspect that the data are the result of an effective PR effort!

Amorphous Alloys

Recently, as a result of work at AlliedSignal and elsewhere, interest has been growing in the production and use of amorphous aluminum, magnesium and other alloys. These are typically produced by rapid quenching of the molten alloy onto a cooled surface. The amorphous or "glassy" metals have a number of very desirable properties including, for example, unusually high corrosion resistance, thought to be due to the lack of surface/grain boundary intersects, but they are somewhat thermally unstable and will recrystallize to a more normal crystalline morphology. The addition of small amounts of rare earths, usually accompanied by transition metals, to the melt prior to 'casting' results in a material that, with carefully-controlled annealing, produces a nanocrystalline (i.e., extremely finely crystalline) structure that is more stable than the amorphous material but has better mechanical properties and equally good corrosion resistance (over-annealing to a more coarse structure offsets these advantages). New uses are rapidly developing for these materials. Once again, the mechanism by which the lanthanide additions exert their effect is not yet known. Typically, addition amounts are less than 1 wt.%, but precise control of both chemistry and processing is necessary.

Galvanizing Applications

Mischmetal is also used very effectively in an improved zinc galvanizing product called Galfan^{TM}(developed by ILZRO/Weirton Steel). This is a zinc-5 wt.% aluminum alloy with small Mm additions that is used as a substitute for 'straight' zinc. It has been shown to be very effective in most galvanize applications with the possible exception of heavily-contaminated industrial environments. It is in extensive use in Europe as a galvanizing treatment for sheet steel.

Mischmetal or pure are earth additions are also surprisingly beneficial in magnesium and aluminum-magnesium cast alloys. Once again, the grain structure is refined, the negative impact of intermetallics on notch sensitivity, toughness and strength is offset and corrosion resistance greatly improved. In some cases (e.g., Al8Mg5), formation of the intermetallic may be suppressed.

The beneficial effects of the lanthanides on the non-ferrous metals extends, not surprisingly, to their metal-matrix composites. Once again, the presence of the rare earths results in grain refinement, improved mechanical properties and, apparently, improved intermetallic morphology in addition to enhanced corrosion resistance.

Numerous other claims for benefits have been made, mostly in the Chinese, and occasionally in the Russian, literature. In most cases, these claims have not yet been substantiated by Western research or practice but there is no reason to doubt their validity, based on the reliability of the work discussed earlier.

2.3 Nuclear Applications of Rare Earth Metals

Europium, gadolinium and dysprosium have large capture cross-sections for thermal neutrons and thus are often incorporated into control rods to regulate reactor operation. Rare earth elements can also be used as burnable neutron absorbers to maintain the reactor flux at a more constant level. Obviously, with the relative demise of the nuclear power industry, this is a small and non-growing market for the rare earth metals.

2.4 Supermagnets and Superconductors

Although not the theme of this article, one of the most important applications of the rare earth elements is in "supermagnet" materials - usually permanent magnets based on gadolinium-cobalt, samarium-cobalt or neodymium-iron-boron with other metals in minor amounts. The cobalt alloys offer the highest permanent magnet performance known. Use of these materials continues to grow rapidly at more than 15% annually as power generating devices in automobiles and aircraft grow smaller and more compact while offering higher capacities. Tight control of purity is required to achieve optimum performance.

A number of intermetallic compounds and oxides containing rare earth metals are being evaluated as so-called high TC superconductors - materials that demonstrate superconductivity (vanishingly low electrical resistivity) at temperatures well above 0 deg. K (absolute zero). Once academic curiosities, these materials now offer considerable promise for use in future industrial high-current devices and generating equipment. Development work in this area appears to be growing exponentially and excellent progress is being made. Once again, purity seems to important in achieving optimum performance.

2.5 Other Metallurgical Applications

While there are many possible metallurgical applications for the RE metals, the high cost of these metals usually results in an alternative choice being made. However, there are some areas, such as those mentioned in sections 5.1 and 5.2, that make use of the unique characteristics of the rare earths. These include uses in thermite devices and in tracer ammunition, both of which utilize the pyrophoric characteristics of these metals to good effect. The high cost of the rare earth metals, even mischmetal, makes it unlikely that they will replace aluminum or (occasionally) magnesium in conventional thermite mixtures for steel rail welding and equivalent uses. However, in view of the favorable effect of rare earth elements on the performance of cast steels (see above), there may be an opportunity to use rare earths together with aluminum or magnesium in sophisticated thermite mixtures for welding applications in which a high performance weld is required. They could be especially valuable for underwater thermite welding systems.

Pyrophoric formulations are also used in a variety of weapons systems (mischmetal has featured in these for many years) such as tracer shells and incendiary weapons of various kinds.

The writers are frequently asked to provide fabricated rare earth samples (wire, tube, sheet) for other unspecified applications. Clearly, other uses for pure rare earth metals are also being investigated.

2.6 Other Uses of the Rare Earth Elements and their Compounds

While this article has intentionally focused on the larger-scale metallurgical uses of the rare earth metals, there are very many uses of these elements that fall into other categories. The total markets for cerium and lanthanum are large since the oxides and other compounds of these metals have found broad industrial application in products that range from camera lenses to polishing compounds. Some of these are still evolving as the technology is improved. For example (and this list is far from comprehensive):

¨ Aluminum-scandium alloys are finding uses in sporting goods such as golf clubs (along with almost any other combination of metals in this fashion-conscious sport!), baseball bats, bike frames, etc.

¨ A wide range of specialty ceramics is emerging, based on rare earth oxides. A comprehensive discussion would require a major publication of its own! Yttria (Y_2O_3) has long been used to stabilize zirconia (ZrO_2) ceramics at high temperature but recent research has uncovered numerous additional applications for ceramics containing rare earth oxides. For example, a "second generation" family of high TC superconductors such as $YBa_2Cu_3O_7$ has appeared which, while very difficult to fabricate into conductors (such as wires) offer some exciting properties. Much of the early work on high-TC oxide superconductors focused on the so-called ABO_3 perovskites such as $LaTiO_3$ and later on layered perovskites such as $(La,Sr)_2CuO_4$. Rare earths are also commonly found in solid-state zirconia-based solid electrolytes used in commercial oxygen sensors (e.g., for automotive use) and in laboratory applications. Rare earth nitride ceramics are also of interest.

¨ The rare earth oxides find wide use as components of catalysts used in chemical processing (for oxidation, amidoxidation, polymerization) and in the treatment of exhaust gases produced by internal combustion engines. They are also to be found in silicone stabilization additive packages, diesel fuel additives (for particulates control) and in corrosion inhibitors.

¨ Heated rare earth metals are used as scavengers or "getters" for oxygen and nitrogen, as well as other gases such as hydrogen, in high-vacuum systems and in nuclear applications (especially those using liquid metal coolants which are highly corrosive in the presence of even minute amounts of oxygen). Hafnium and zirconium also serve well in this application.

¨ Recent work at the DOE Ames Lab and elsewhere has shown the potential of using tunable magnetic regenerator intermetallics such as $Gd_5(Ge_2Si_2)$, which exhibit so-called 'giant magnetocaloric effects', as the basis for magnetic refrigeration systems.

¨ Neodymium, scandium and lanthanum are used in sodium discharge lamps to moderate the yellow coloration of the light generated by these. Rare earth oxides were also used for many years to coat filaments in vacuum tubes, but this market has almost disappeared.

¨ Radioactive yttrium and terbium wire are used in medicine as implants for cancer therapy (e.g., in the so-called 'gamma-wire' therapy).

¨ Several of the rare earths - lanthanum, praseodymium, for example, are being used in 'new generation' long-life metal/hydride batteries.

¨ Chinese workers claim that certain of the RE metals are useful in agriculture, perhaps as plant growth stimulators. This has not yet been confirmed by European or U.S. work. China is the world's largest rare earth producer so it is possible that such claims are premature and the result of excessive marketing zeal!

2.7 Toxicology of the rare Earths

There appears to have been little systematic work on the toxicology of the rare earth metals and their compounds. Insufficient data is available even to complete MSDS sheets on most shipments of RE products. The pure metals (primarily Y and Tb) have seen limited use a medical implant materials and the literature has general references to the metals as benign and harmless but this does not seem to be completely in keeping with the known reactivity of these metals. More work is needed in this area. Meanwhile, the RE metals and compounds should be handled circumspectly.

3. Future New Uses for Rare Earths

3.1 Pure Rare Earth Metals or Alloys

Extraction and Refining

Better definition of the mechanical and physical properties of the rare earth metals might eventually lead to additional uses of these metals in pure or alloyed form, but only if lower-cost methods of extraction (from the mineral concentrates, which are relatively inexpensive) and purification of the metals can be developed. RE compounds such as the oxides are available in moderate purity, although even these require extensive and repetitive ion exchange processing (as soluble salts) before they are sufficiently well separated from compounds of other rare earths. The oxides are then easily produced at acceptable purity levels (e.g., 5N or better). Arris International supplies 6N oxides for most rare earth metals. However, although there is a demand for ultra-high purity (e.g., 7N) oxides, these are not readily available.

Metallothermic reduction of a suitable compound (such as the RE chloride or, more often, fluoride) using 10% excess calcium in a helium or argon atmosphere can then be used to produce a relatively crude metal that is loaded with both halide atoms, calcium and often oxygen. The resulting metal is extremely impure and therefore brittle. Mischmetal is produced in this way from the unseparated oxides or halides, but is seldom further refined.

The high purity metal that is required for research purposes and for the few commercial uses for which the single RE metals are needed can then be obtained by one of several methods:

- Vacuum remelting at very high vacuum, usually in a tantalum crucible (many of the more serious impurities evaporate); several techniques are used depending on the vapor pressure of the metal being refined. The high-melting, high-VP metals such as thulium can be purified by sublimation.

- Floating-zone refining, again in high vacuum. This has much the same effect but results in a more pure product and, when fully developed (which is far from easy!) is less costly.

- Electrochemical refining using a molten fluoride or chloride electrolyte with the crude metal as the cathode (it can be solid and contained in a titanium or tantalum basket) and a carbon anode. Very high purity metal can be produced in this way with little or no re-contamination of the metal with fluorine or chlorine provided that the refining potential remains 'on' while the cell is cooled. It remains to be seen whether this technology, which borrows heavily from aluminum and magnesium production and refining, can be scaled up economically.

- It is also possible that the rare earths could be all of extracted (from the oxides or halides), separated and purified electrochemically in a multi-step process. This is being evaluated by the authors.

The Pure Rare Earths

Once adequate mechanical and physical property data are available and pricing can be projected for production in significant volume (in this context, kilograms rather than grams) decisions can be made regarding potential new applications. However, it is difficult to see which materials could be replaced by any of the pure rare earths. The latter offer none of the advantages of Al, Mg or Ti (low density and excellent oxidation resistance) or steels (strength) and are available only at higher cost. However, they seem to be able to play a very valuable role in improving the properties and therefore extending the service limits of these almost ubiquitous materials. Perhaps in this context, the RE metals will be "always the bridesmaid, never the bride".

"Pure" Mischmetal

One possible exception to this rule may be mischmetal (Mm). Alloys of the rare earth metals generally (but not universally) behave a little like a pure rare earth. Thus mischmetal, which, depending on source, may contain up to 70 wt.% of Ce + La (which reportedly form a continuous series of solid solutions) plus about 20-25 wt.% of other rare earths and 5-10 wt.% iron, may, once the iron and interstitials are removed, offer the performance of a pure rare earth without the high cost of separating the rare earth components. Documentation of the properties of mischmetal in almost any condition of purity are lacking so it is, once again, not yet possible to support this conjecture.

3.2 Rare Earths in Alloys

In their various supporting roles, the future of the rare earth elements looks bright indeed. Recent data on their effectiveness in improving the mechanical performance, fatigue resistance and also corrosion resistance of a growing variety of aluminum-, magnesium-, zinc and iron-based alloys, including the stainless steels, are very persuasive. The only possible downside seems to be the lack of any in-depth understanding of the mechanisms by which these improvements are achieved. Experience suggests that wide commercial use of any new technology without a sound technical foundation can lead to catastrophic results (the use of aluminum alloys in pressurized jet aircraft in the 1950s before an understanding of fatigue mechanisms was developed is one example). Thus Arris International, with others in the rare earth materials industry, will be focusing in the near future on developing a better understanding of the mechanism by which rare earth metals control alloy morphology and facilitate the development of enhanced corrosion resistance in these alloys. In the process, new alloy formulations will undoubtedly result, since this work is at such an early stage.

4. Summary: Bright Future!

Given the quantities involved, it seems likely that the future market for master alloys based on the rare earth metals will be both large and fast-growing. Other promising uses are the high-Tc superconductors, metal-hydride batteries and the permanent magnet market. In this article, we have largely ignored the markets for rare earth compounds, especially the oxides, but these are already very large and growing rapidly. Fortunately, the rare earth minerals are widespread and plentiful and the present supply will take care of any foreseeable demand for many years to come. Technology now under development will result in needed cost reductions for many rare earth products and will promote the emergence of many new markets. The future looks bright!