Recycling of Rare Earth Magnet Scrap

During the manufacturing process for rare earth magnets, a rather high percentage of the starting material ends up as scrap. By one estimation, 2400 tons of scrap have been produced in manufacturing 5500 tons of magnets. Of this scrap, less than 10% was recycled. This low recovery rate reflects the difficulty in effectively recycling a highly reactive material. Recycling of Sm-Co scrap is more common than Nd-Fe-B scrap, not because of the RE, but because it is relatively easy to recover the Co, making the process economically viable. Some of the problems associated with recycling Nd-Fe-B are presented by a group of authors in a pair of papers, K. Asabe et al. and R. Suzuki et al. {*Mater. Trans.*, **42**, [12], 2487-91 (2001)} and {*Mater. Trans.*, **42**, [12], 2492-8 (2001)}. Manufacturing scrap consists generally of two types, grinding residue or sludge and magnets, which have defects such as chips or coating failures. While broken sintered magnets may be viewed as relatively high value scrap, recycling them is not as simple as remelting the material due to the fact that the magnets have usually been coated either by metal plating or by organic materials. Oxidation and polymer coatings may raise the oxygen and carbon content of this material above acceptable levels. The case is much worse for grinding scrap that is inevitably heavily oxidized and contaminated with cutting oil and residue from the grinding media, which may include diamond grit and polymer binders. The two major problems in processing both types of scrap that are considered in these papers are the removal of carbon and the removal of oxygen. The approach that they take is to decarburize the material by oxidation of the C to CO_2 and then perform a two step reduction of the oxidized metal powders. H_2 reduction is used to reduce the Fe in the material, while Ca is used to reduce the RE. The most complex treatment is for grinding scrap or sludge. Following the removal of the grinding residue by solvent washing in butanol, the material was then dried at 353 K for 86.4 ks (80°C for 24 hrs) in air. The dried grinding sludge has a 1.1 μm particle size and analyzed oxygen content of 5.6 wt %. X-ray diffraction of the powder shows that it is mainly $Nd_2Fe_{14}B$ despite the fact that the oxygen content is enough to fully oxidize all of the RE. (While the authors note this anomaly, they do not attempt to explain it. The probable cause is surface absorbed water. Water is extremely difficult to remove from the surface of Nd_2O_3. Nd_2O_3 that has been dried at 500°C will undergo an additional 2% weight loss when dried at 900°C.) The dried powder was oxidized in air by ramping the temperature at 10°C/minute to 1000°C where it was held for 3 hrs. Through a series of experiments, the authors determined that there was sufficient oxygen in the powder to decarburize the powder in vacuum with no additional oxygen. While carbon will burn out at much lower temperatures, the high temperature was probably required to reduce the RE carbides. This process reduces the carbon content to an acceptable level but results in a powder that is heavily oxidized. The oxygen content corresponds to full oxidation of at least 85% of all constituents. The first step in the reduction of the oxide powder is H_2 reduction at 1000°C for 1 hr, which results in $NdFeO_3$ and Fe. The reduction of the $NdFeO_3$ was carried out using Ca. Ca vapor was tried in order to avoid excess Ca, but a CaO layer formed on the surface. Liquid Ca and liquid Ca + $CaCl_2$ were also investigated. Since CaO is soluble in $CaCl_2$, the initial experiments used enough $CaCl_2$ to dissolve all of the CaO. However, it was determined that only a small amount of $CaCl_2$ was required. Presumably, the CaO on the surface of the powders was dissolved in the $CaCl_2$, and subsequently precipitated as large $CaCl_2$ grains. Finally, a series of complicated washing steps were used to dissolve the CaO and $CaCl_2$.

While this process works well, it does not address one problem which is common to all recycling schemes for Nd-Fe-B. Every manufacturer of Nd-Fe-B has numerous compositions with various additions. If the scrap is

not separated, the recycled alloy will have highly variable composition with the possibility of non-compatible alloy additions. From a materials standpoint, it is quite possible that extensive recycling of scrap may never be economical. However, the authors point out that there is a growing possibility that the scrap will become classified as hazardous waste. If this happens, the cost of waste disposal may trip the economics in favor of recycling.
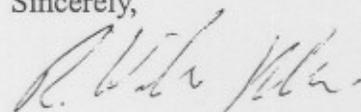
Dual Wavelength Lasing Cr:Er:Tm:Ho;YAG

For many applications, a laser of a specific wavelength is required. This appears to be particularly true of medical applications where energy absorption is directly related to the wavelength dependence of the absorption spectrum of water. For dental applications, high absorption is desired, while for soft tissue applications deeper penetration that comes from lower absorption is required. Recently, B. M. Walsh et al. {*J. Appl. Phys.*, **91**, [1], 11-17 (2002)} have developed a co-doped Yttrium Aluminum Garnet, YAG laser, which may be operated at 2.1 and 2.9 μm by simply adjusting the length of the flash lamp pulse. This, in principal, will allow a single laser to be used in both hard and soft tissue procedures. While the details of the laser construction are probably not of general interest, the introduction provides an informative glimpse of medical requirements, and the discussion of the operation of the laser provides insight into the physics of lasers. The co-doping of the YAG is relatively straight forward though looking at the formula you might expect at least four wavelengths. In practice, only the Er and Ho provide the light output. The additional dopants are required in order to efficiently populate the appropriate Er and Ho energy levels with the pump lamp. The ability to tune the laser by varying the pulse duration of the flash lamp results from very different lifetimes for the Er and Ho excited states and the details of the energy transfer. For a short pulse <200μs, only the Er is excited, while for a pulse length of >500 μs only the Ho is excited. For intermediate times, both transitions are active. Careful design of the mirrors and dual wavelength reflective coatings are required to construct a cavity that will resonate at both wavelengths. The paper provides a nice discussion of the problems involved in laser design for a fairly broad audience.

Bulk Nanocomposite Permanent Magnets

In order to produce a high strength permanent magnet, both a high saturation magnetization and high magnetocrystalline anisotropy are required. Unfortunately, these appear to be competing rather than complimentary properties so that in an essentially single-phase material, a compromise must be reached in order to obtain the maximum energy product. In nanocomposite permanent magnets, a hard magnetic phase is exchange coupled to a soft phase with high saturation. In this case, the hard phase imparts anisotropy to the nanocomposite, while the soft phase enhances the magnetization. Of course, there is still a compromise as the soft phase reduces average anisotropy, while the hard phase reduces the magnetization. However, significantly enhanced magnets can be obtained. The problem is that the length scale over which the exchange interactions are effective is in the nanometer range. Thus, this type of magnet is generally prepared by crystallizing an amorphous precursor. Precursor preparation requires rapid solidification that produces thin ribbons or fine powders. These materials are then used in bonded magnets. As a result, the density of magnet material is only about 60-70%, which reduces the maximum energy product by 50-60%. W. Zhang and A. Inoue {*Appl. Phys. Lett.*, **80**, [9], 1610-12 (2002)} have now produced a nanocomposite magnet by the devitrification of a bulk metallic glass. The alloy $Fe_{67}Co_{9.4}Nd_{3.1}Dy_{0.5}B$ can be produced by injection casting into a $0.5 - 1.0$ mm copper mold. Samples that are found to be amorphous, using TEM bright field imaging, have been produced in 12 mm lengths. The composition is such that upon devitrification a nanocomposite of $Nd_2Fe_{14}B$, $(Fe,Co)_3B$ and $\alpha(Fe,Co)$ is produced. Under appropriate annealing conditions, 913 K for 600 s, a bulk magnet with an 11.6MGOe energy product can be produced.

Sincerely,

R. W. McCallum