

New Protective Coatings for Rare Earth Magnets Prevent their Corrosion and Oxidation

Commercial rare-earth alloy powders such as neodymium-iron-boron (Nd-Fe-B) or "neo alloy" powders are produced by crushing melt-spun neo alloy ribbons into platelets with varying sizes and distributions (mean particle size approximately 200 μm). The neo alloy powders produced by this method are highly sensitive to moisture and oxidize readily in air. The spherical neo alloy powders (mean particle size approximately 40 μm) made by high-pressure gas atomization are even more sensitive to fluctuations in the moisture and temperature.

When heated in air at high temperatures, the reactivity of the gas-atomized powder increases, which may be due to its higher specific surface area. The thermal oxidation of neo alloy powders is due to their direct oxidation in air and is exacerbated in the presence of an aqueous electrolyte. In general, oxidation rates are low at air temperatures below 150°C. However, very high oxidation rates can be produced in humid environments. The rapid attack occurs via the preferential consumption of Nd- and B-rich phases on the grain boundaries, which causes the grains of the ferromagnetic phase to loosen. This, in turn, diminishes the structural integrity of the magnet.

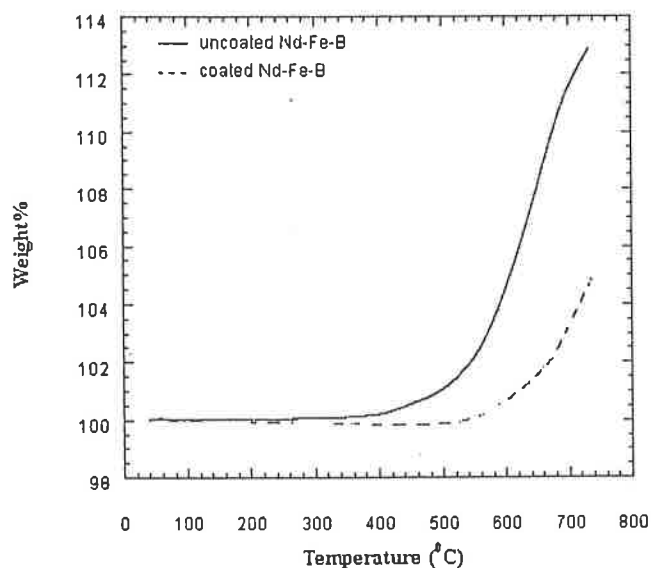


Figure 1. Thermogravimetric analysis (TGA) curves of coated and uncoated commercial neo alloy powder heated in air.

Because of high remanent induction (magnetic induction that remains after removal of the applied magnetizing force), magnetic flux density, and high performance value, neo alloys are widely used for making both permanent (metallic) and bonded magnets. Researchers at Iowa State University have successfully developed an impervious coating system for rare-earth alloys such as the neo alloys, which prevents their thermal oxidation and absorption of moisture. It is anticipated that coated neo alloys will find many uses where these magnets are exposed to humidity and high-temperatures, such as in automotive and computer hardware applications. They could also be used to make electrically conductive plastic alloys.

Uncoated commercial neo alloys as well as those produced via high-pressure gas atomization become very corroded in humid and high temperature environments. The coating system developed at Iowa State is composed of an organometallic compound with dual chemical functional groups that reacts spontaneously with the neo alloy powders and coats the surface of the powder particles with a molecular layer of the coating compound. As indicated in Figure 1, the coated powder is water-resistant and thermally stable up to 500°C. Three classes of organometallic compounds (a metal is attached directly to a carbon) with the general formula $R-X-(OR')_n$ — where R and R' are alkyl (paraffin hydrocarbon) groups, X is Si, Zr, or Ti, and n is 3 or 4 — are being investigated. Thus far, coating agents with the general formula $R-Si-(OR')_n$ have been shown to be the most promising.

In the coating process, the neo alloy powders are immersed in an aqueous solution of the coating agents, followed by ultrasonic homogenization for five minutes to enhance wetting. After the coating treatment, the excess solution is decanted and the coated powder is dried (at 80°C in a 350 MPa vacuum oven). The method of applying the coating agents to the neo alloy powders is essential for achieving optimal results. The environmentally benign nature of the coating solution (about 1 g of the liquid coating agent in 100 g of the aqueous solvent) and the ease of the coating process is expected to make it possible to coat the powders in situ during melt spinning, followed by crushing of the neo alloy ribbons and high-pressure gas atomization of the neo alloys.

The Iowa State researchers are exploring the effects of their coating system on the processability and magnetic properties of plastic magnets. Conventional methods of polymer processing are used to fabricate these magnets, which are composed of polymer matrices and magnetic fillers including hard ferrites of the Ba and Sr systems, alnico (a permanent magnet alloy of Fe, Al, Ni, and Co), and rare earth magnetic systems such as SmCo_5 , $\text{Sm}_2(\text{Co, Fe, Cu})$,

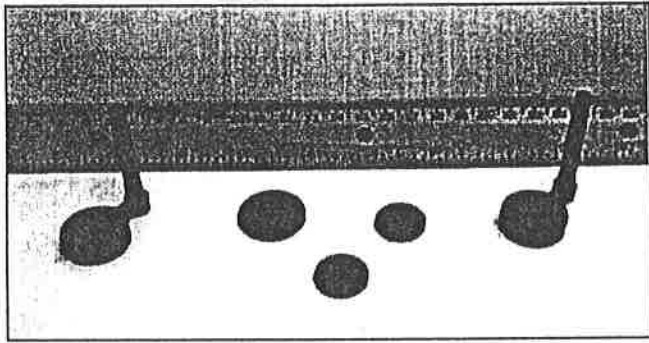


Figure 2. Injection molded samples of 60 volume % neo alloy/PPS plastic magnets.

Zr₁, and Nd₂Fe₁₄B alloys.

Plastic magnets are highly advantageous with respect to their cost effectiveness and their ability to be fabricated into complex shapes compared with their metallic and ceramic counterparts. They are made by blending a magnetic filler with a polymeric binder in a mixer or extruder. Using conventional polymer processing methods such as injection molding, the resulting composite material can be formed into magnetic components with complex shapes, shown in Figure 2. Neo alloy plastic magnets can be used in electromechanical devices where energy efficiency is a prime concern such as in automotive applications. The advantages of the plastic magnets over their metallic and ceramic counterparts include low weight, resistance to corrosion, ease of machining and forming, and capability for high production rates. These advantages of plastic magnets make them useful for sensors, toys, computers, and numerous other communications applications that require miniaturized parts with precise and complex shapes and structures.

At present, the low energy product (BH)_{max} and poor heat resistance properties of commercial plastic magnets limit their processability and applications. Heat resistance can be

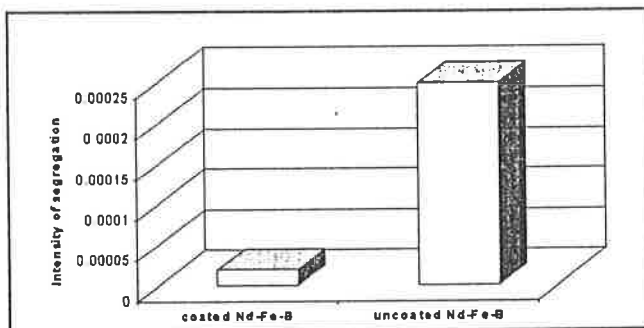


Figure 3. The effect of the coating agent on the intensity of segregation of commercial neo alloy powder in PPS at equal volume loadings of the neo alloy powder. A 0 intensity of segregation means perfect mixing and an intensity of segregation of 1 means no mixing.



(a)

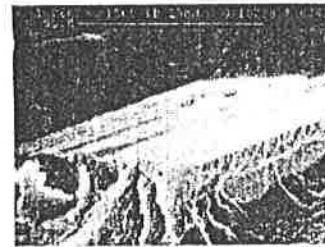


Figure 4. Scanning electron micrographs of commercial neo alloy powder/PPS magnets: (a) uncoated and (b) coated.

improved by selecting heat resistance binders and high temperature polymers. The polymer, poly(*p*-phenylene sulfide) or PPS, is an optimal material for fabricating bonded magnets because of its desirable combination of properties including good thermal stability, low viscosity, and resistance to chemical environments. Two other polymers, poly (ether sulfone) and poly(phenylene sulfone), have also been

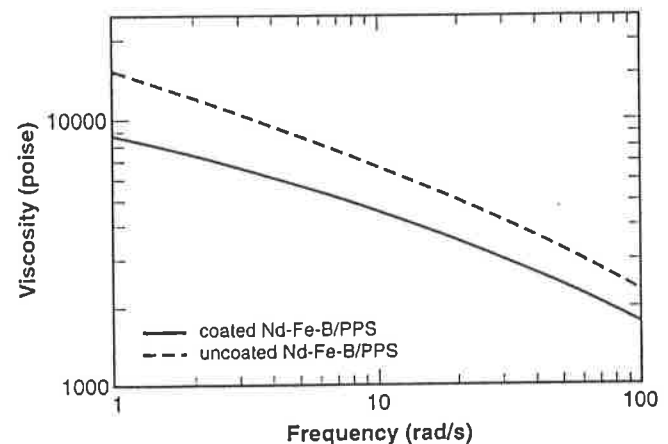


Figure 5. A comparison of the effect of the coating on the viscosity of melts of 15 volume % coated and uncoated neo alloy powder/PPS composites at 290°C indicates a reduction in viscosity in the composites made with the coated powder..

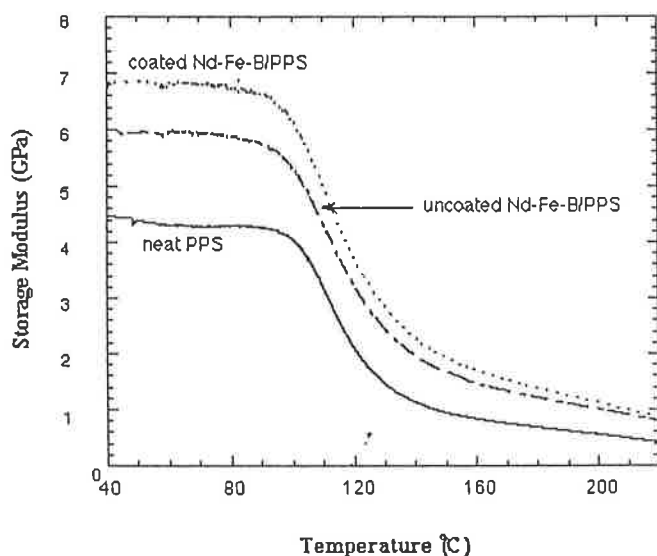


Figure 6. A comparison in a three-point bend test of the elastic properties (storage modulus) as a function of temperature of pure PPS, a 15 volume % coated neo alloy powder/PPS composite, and a 15 volume % uncoated neo alloy powder/PPS composite.

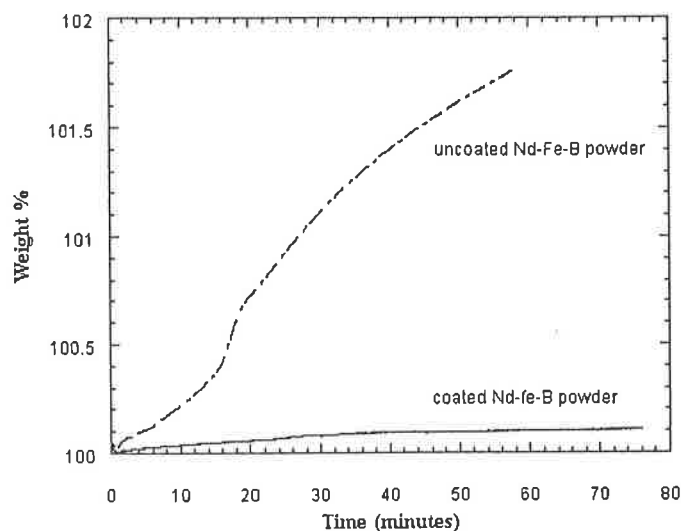


Figure 7. The percent change in weight as a function of time (TGA curves) of coated and uncoated commercial neo alloy powder heated in air at 400°C.

identified as potential polymer matrices for high-temperature plastic magnets. However, their high viscosity needs to be modified to allow the high volume loading of the neo powders required for maximum magnetic properties. Under normal use temperatures ($\leq 180^{\circ}\text{C}$), the corrosion of neo alloys in the PPS-bonded magnets is significantly reduced by the use of the coating agent and polymer binder. At temperatures above the decomposition temperatures of the organometallic coating compound and the polymer, the corrosion mechanism of the pure neo alloys predominates.

The magnetic pathways in plastic magnets critically depend on the relative association of the magnetic neo powders and their level of dispersion. Mechanical properties such as fracture toughness and strain to failure under tensile deformation are also very sensitive to the state of the powder dispersion. Therefore, the degree of mixing is a critical factor in controlling the magnetic and mechanical properties of plastic magnets (see Figure 3). The surface modification of neo powders with this new coating agent, shown in Figure 4, improves their dispersion by making their surface more hydrophobic and compatible with the polymer. This enables the powder to chemically bond to the polymer through hydrogen or ionic bonds.

The improvement in the degree of mixing of the coated powders indicated in Figure 3 is attributable to good wetting, which is also evidenced by the reduced viscosity of the coated neo alloy-plastic magnets, shown in Figure 5. These factors also enhance the processability and corrosion resistance of the plastic magnets. In addition, pretreating the

powders with the coating agent (prior to incorporation into the plastic matrix) improves the mechanical properties of the plastic magnet as indicated in Figure 6.

To understand the flow behavior of these plastic magnets, their rheological properties were measured at low concentrations of 2 volume % to 15 volume % of neo alloy/PPS magnet. The results confirmed that the presence of a monolayer of the coating agent on the surface of the powder reduces the viscosity of the suspensions, as shown in Figure 5, and also that the particle size distribution of the powder has a major effect on the rheological properties of the magnetic powder suspension. It is believed that the beneficial effect of the coating agent is due, in part, to good wetting of the magnetic powders. Morphological and chemical analysis data appear to support this interesting wetting phenomenon.

The research conducted thus far has shown that the difficulties of processing plastic-neo alloy magnets for high temperature uses can be minimized or even eliminated by using these coating agents to coat the surface of the powders prior to incorporating them into the polymer matrix. Because the dispersion of the neo alloy particulates in the continuous polymer matrices is improved, the neo alloy powder loading can be increased without increasing the bulk viscosity of the composite. The coating agent apparently forms an impervious monolayer or a passivation layer on the surface of the powders that markedly improves their oxidation resistance. As shown on Figure 7, this is particularly true at high temperatures.

Furthermore, the chemical nature of the coating agent

Table 1. The Effect of the Coating Agent on the Maximum Energy Product of Commercial Neo Alloy/PPS Magnets

Sample No.	Volume Fraction, %	Maximum Energy product, MGOe
Filler: uncoated MQP-O powder *		
1	38.7	1.985
2	38.9	2.08
3	39.1	2.12
Filler: coated MQP-O powder		
4	37.3	1.975
5	38.3	2.07
Filler: uncoated gas-atomized NdFeB powder		
6	37.8	0.629
7	35.7	0.547
Filler: coated gas-atomized NdFeB powder		
8	36.5	0.548
9	36.7	0.582

selectively allows wetting of the coated powders by the polymer and good adhesion between the coated magnetic powders and the polymer in the bonded magnet. Confirmation of the homogeneous coating of the powders with the chemical coating agent was obtained by scanning electron and Auger microscopy. Thermogravimetric analysis results shows that the uncoated neo alloy powder is more stable than the uncoated gas-atomized powder, while chemically coating both powders increases their thermal oxidation stability. The researchers believe that coating the ultrafine neo alloy powders will make them thermally stable enough to be practically useful, and thus increase the efficiency of the neo alloy powder production process.

The thermal oxidation corrosion resistance of the coating agent was determined by measuring the energy product $(BH)_{max}$ of the PPS bonded neo alloy magnets containing the coated and uncoated powders. The measurements showed that the $(BH)_{max}$ of samples containing gas-atomized neo alloy powders was significantly lower than that of the bonded magnets containing commercially produced powders. As shown in Table 1, modifying the powder surfaces with the chemical coating agent produces magnets with higher energy products than the magnets containing identical volume fractions of the uncoated powders. These results are consistent with the observed improvement in the thermal oxidation resistance of bonded magnets made with the coated powders.

The researchers believe that their coating system should make it possible to fabricate permanent magnets and high-temperature plastic magnets for use in hostile and corrosive environments where the present commercial magnetic rare-

earth alloys cannot be used. They also believe that the surface treatment they have successfully demonstrated for PPS-bonded neo alloy magnets could be readily adapted for other types of plastic magnets, thereby leading to the development of useful new magnetic devices. The results achieved thus far with coated neo alloy powders and plastic neo alloy magnets indicate that both are suitable for load-bearing applications in high temperature and aggressive environments where commercial uncoated permanent (metallic) neo alloy magnets cannot be used. The researchers plan to apply their coating technology to a wider range of special magnetic rare earth alloy-high temperature plastic magnets than the ones investigated to date.

Iowa State University is seeking industrial partners to license their patent pending method for making water-resistant, temperature-resistant neo alloys and plastic neo alloy magnets for use in high temperature and corrosive environments.

Source: For the technology: Prof. Joshua Otaigbe, Iowa State University of Science & Technology, 3053 Gilman Hall, Ames, IA 50011 Phone: (515) 294-9678. Fax: (515) 294-5444. E-mail: otaigbe@iastate.edu. For licensing: Mary Kleis, Office of Intellectual Property and Technology Transfer, Iowa State University, 310 Lab of Mechanics, Ames, IA 50011. Phone: (515) 294-4740. Fax: (515) 294-0778. E-mail: mkleis@iastate.edu

Tough, Lightweight, Superinsulating Aerogel/Tile Composites have Potential Industrial Applications

Pure aerogels are extremely lightweight and exceptionally insulating porous solids that can be made of silica (SiO_2), alumina (Al_2O_3), carbon, or other materials. Sometimes described as "solid smoke," their industrial applications have been limited due to their low strength and high brittleness. An aerogel composite tile made by partly filling spacecraft insulation tiles with a layer of aerogel has been invented at NASA's Ames Research Center that has the advantageous thermal and physical properties of aerogels while maintaining the strength and other proven advantages of the space shuttle tiles. The new aerogel /tile composite is the first form of an aerogel that can be coated, cut, machined, drilled, and attached to a surface, making it useful for commercial insulation for furnaces, refrigerators