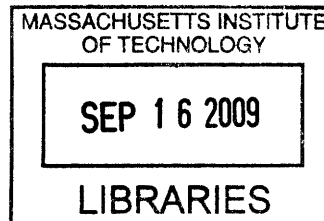# Electrically Insulating Phosphate Coatings for Iron Powder Based Electromagnetic Core Applications

by

William Rane Nolan

Submitted to the Department Of Mechanical Engineering
in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Science in Mechanical Engineering
at the
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Submitted to the Department Of Mechanical Engineering
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ABSTRACT

Powdered metals, such as iron, are a common building block for electromagnetic cores. An iron powder was reacted with phosphoric acid to create a layer of iron phosphate on each particle. This electrically insulating phosphate layer could lead to significant reductions in eddy current losses in alternating current applications. The electro-magnetic properties of this phosphate-coated powder material were examined as a function of heat treatment. Additionally, SEM and EDS were used analyze the particle interfaces and composition in compressed bar-shape samples that were heat treated at temperatures ranging from 315°C to 540°C. The bulk composition of oxygen and phosphorus are also tested for each heat treatment. Results indicate that after high temperature heat treatments (required for stress reduction, sintering, increased magnetic permeability, and decreased coercivity), the bulk resistivity is reduced. Correlation of interface structure and composition with these trends in resistivity is discussed. Ultimately, this analysis will aid in the development of coatings that withstand higher temperatures and yield ideal properties for electromagnetic core applications.

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Title: Associate Professor of Metallurgy

Biographical Note

The author attended the Massachusetts Institute of Technology from September 2005 to June 2009. He is a member of the Pi Tau Sigma and Tau Beta Pi engineering societies. Elements of the research presented in this thesis were presented by the author at a symposium of the Minerals, Metals, and Materials Society annual meeting, February 2009 in San Francisco. The author was accepted by the University of Cambridge and will pursue a PhD there, researching supersonic inlet flow control, beginning October 2009.

Acknowledgments

Table of Contents

Introduction

Manufacturing parts from iron powders is most often done for economic reasons.[1] This is remarkable as the production of powder typically is done after refining iron ore in a traditional steel making process; the additional step of converting ingots into powder is a significant expense.

The viability of powder metallurgy (PM) methods is therefore generally seen in the manufacturability of parts. PM processes are often far more efficient in the use of raw materials. Many traditional manufacturing techniques machine and remove material from an initial billet to form the desired part. For a PM process, the powder is compacted directly into the shape of the part, or, if not, significantly less machining is required to complete the part. The better material usage, with less scrap after manufacturing, and simplicity of pressing parts of complex geometries often outweigh the added cost of manufacturing powder.

For electromagnetic applications, the convenience of pressing iron powder directly into electromagnetic cores may be compounded with the possibility for improved electromagnetic characteristics over conventional laminated steel cores.[2]

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[1] Dowson (1990), p 11-12.
[2] Hanejko et al. (1996).

5

Manufacturing PM Powders

Many iron powders are created through a process in the industry known as atomization. This general process describes the production and solidification of droplets from a molten stream. A variety of methods for both producing and solidifying the molten droplets have been devised. Since surface tension in the droplets acts to make them more spherical in shape, the droplet size and solidification rate of the manufacturing process affect the end product. Slow cooling rates allow droplets to freeze as spheres, while quicker cooling rates or high energy impacts with solid surfaces result in highly distorted and complex particles geometries. Highly irregular powders are more widely employed, for they are able to interlock and result in stronger compactions.[3]

Water atomization is the most widely employed process for producing PM powders because the quenching capability of water yields desirable, irregular powders.[4] The essential premise of water atomization is that the impact of one or more jets of water onto a stream of molten metal will disintegrate and rapidly freeze powder particles. Numerous variations of equipment, geometries, and nozzle pressures abound, but typically higher jet velocities and flow rates result in finer and more irregular powders. Figure 2 illustrates the irregularity of a commercially-available, water-atomized steel.

During production, the water is drained from the powder, and the powder is then dried in a convection oven, sometimes under partial vacuum.[5] The introduction of water to molten metal inevitably leads to oxidation on the surface of the powder, which can be removed via a reduction treatment.

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[3] Smith (2003), p 21-24.
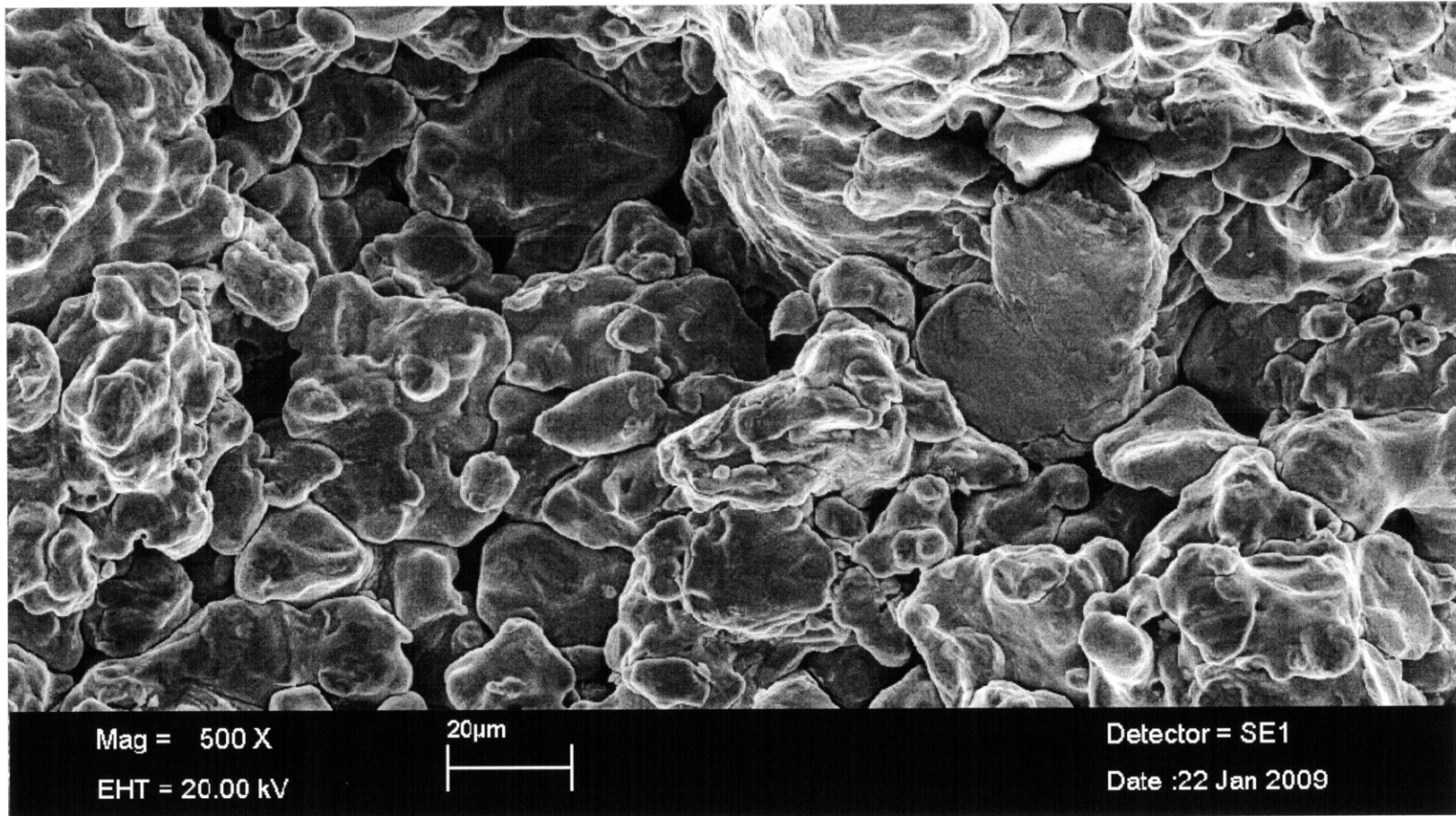[4] Dowson (1990), p 25.
[5] Dowson (1990), p 27.

Figure 1. SEM image illustrating the irregular shapes of water-atomized iron powder. This image is of the fracture surface of a sample processed and pressed as described in the Experimental Procedures section and heat treated at 540°C.

Developing PM for Electromagnetic Applications

Heat-treating of compacted powder parts is required to sinter the powder to increase strength and to relieve cold work induced by the compaction. The density of the compact increases at higher heat-treatment temperatures as sintering between powder particles reduces porosity. This effect of increasing density and relief of cold work-induced strain improves the electromagnetic properties of the iron powder.[6] The magnetic performance of the PM material improves, indicated by increased magnetic permeability and decreased magnetic coercivity.

Resistivity is another significant electromagnetic characteristic. Alternating electric fields (as in an induction motor) applied to a core generate eddy currents in the core.[7] This induced current reduces efficiency by resisting magnetization of the core and causing Joule heating. Eddy current loss is proportional to a variety of geometric, material, and experimental parameters, such as,

$$Eddy\ Current\ Loss\ \propto \frac{d^2B^2f^2}{\rho}, \qquad (1)$$

where d is the thickness of the material, B is the magnetic induction, f is the frequency of applied magnetic field, and ρ is the resistivity.[8]

For traditional PM materials, while the size of each powder particle is small, the low particle-particle contact resistance effectively makes a compaction of powder one electrical domain (of large dimension, d) of low resistivity. If the particle-particle contact resistance were to increase substantially, however, each powder particle would behave as its own electronic domain,

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[6] Hanejko and Ellis (1999).
[7] DOE Handbook (1992).
[8] Hanejko et al. (1996).

reducing *d* to the size of powder particles. This dimension is far smaller than traditional laminated steel and iron strips and therefore eddy current loss would be reduced.

One method of increasing the contact resistance of iron powder is to react the powder with phosphoric acid to create a layer of iron phosphate on each particle before the powder is compressed into the final product.[9] While the magnetic properties of the iron substrate improve with higher temperature heat-treatment, the bulk electrical resistivity of the treated powder compact diminishes. Presumably, the iron phosphate insulation is diminishing with heat-treatment. An analysis of the microstructural evolution of the insulated iron powder as a function of heat-treatment will aid in the development of coatings that withstand higher temperatures and yield ideal properties for electromagnetic core applications.

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[9] Narasimhan et al.

Experimental Procedures

A water-atomized powder, Ancorsteel 1000C produced by Hoeganaes Corporation of Riverton, NJ, was used as the base iron powder. The powder is unalloyed and relatively pure (approximately 99.7% iron), and most particles are between 45 and 150 micrometers in size.[10]

The powder was mixed with a solution of phosphoric acid and acetone. Two masses of acid were mixed with the iron: 0.1% and 0.2% of the overall mass of the mixture consisting of iron, acid, and lubricant. The acid was diluted with acetone (approximately 20:1) to promote even wetting of the iron powder. Both the acid solution and iron powder were heated to approximately 45°C before mixing. After several minutes of stirring, the reacted powder was left to finish drying for several hours at room conditions. These prepared powders treated with 0.1%wt and 0.2%wt phosphoric acid are hereinafter referred to as mixes 1A and 2A, respectively.

The final preparation of the mixture involved stirring in 0.75%wt N,N' ethylene bis-stearamide (trade name: Acrawax C), a lubricant that improves the density achieved when compacting the mixture. The prepared powder was then sifted through a 60 mesh (250 μm) screen and tumble mixed for 20 minutes to ensure uniform mixing.

The two mixes were pressed into bars of dimensions 31.8 mm x 12.7 mm x ~6.3 mm at room temperature under pressure of 760 MPa. The thickness was measured for each bar to account for variations in bar mass and natural variations of compressibility. The bars were then heat-treated

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[10] Ancorsteel Datasheet, Hoeganaes Corporation.

in an oven flushed with nitrogen for one hour at temperatures ranging from 315°C to 540°C.[11] The bars cooled for one hour in a cooling zone of the oven also flushed with nitrogen.

Various tests were then conducted on the heat-treated bars.

Bulk electrical resistivity of the bar was measured using the four-terminal method. Note that this measured resistivity is not ρ of equation 1 if each powder particle is modeled individually for eddy current loss. The bulk resistivity is a measurement of both the iron substrate resistivity and the particle-particle contact resistance.

Samples of crushed, heat-treated bars were chemically analyzed. The bulk composition of oxygen and nitrogen were tested using a LECO gas fusion analyzer. The bulk phosphorus content was found using a wet chemical method.

Samples prepared from mix 2A were also examined microstructurally. Bars were cross-sectioned with a diamond saw and hand ground with wet grit paper. (The relatively low temperature heat-treatments did not fully sinter the bars; they could be crumbled under many traditional, easy preparation techniques). To further polish the samples, a Vibromet vibrating polisher using 1 micron suspended aluminum oxide polished them for approximately ten hours. A final polish for 15 minutes using a 0.05 micron suspended aluminum oxide polish completed the preparation. No chemical etchant was used because it was not known how the etchant would affect the iron/phosphorus microstructure. The samples were typically stored under vacuum to protect them from oxidation and to draw out water and solvents from the polishing process.

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[11] This temperature range is well below traditional sintering temperatures for PM materials, which can be in excess of 1000°C.

The compacted microstructure of polished cross-sections of the bars was examined under optical and scanning electron microscopes. Energy-dispersive spectroscopy (EDS) was used to examine the chemical composition (primarily phosphorus content) on the microscale.

Finally, powder from a finely crushed, heat-treated sample was mounted on a lacey-carbon mesh and viewed under a transmission electron microscope (TEM). Due to the low strength of the bars, they could not be dimpled and ion-etched to create a thin cross-section without the cold work of crushing.

Results

<u>Electrical Properties.</u>

The bulk resistivity is reduced after high temperature heat-treatments. The resistivity dropped approximately by a factor of 20 when heat-treated at 455°C compared with 430°C. When treated above 455°C, the resistivities continued to decline, though much less dramatically. The resistivities observed with mix 1A are approximately one-third those of mix 2A. (see Figure 2)

<u>Chemical Composition.</u>

No trend is observed in bulk phosphorus content versus heat treatment (see Figure 3).

High nitrogen content was recorded for powder that was not heat-treated. The nitrogen content was lower and relatively consistent between various heat-treated samples and for samples not heat-treated and not containing Acrawax lubricant. Nitrogen content was nearly identical between mixes 1A and 2A (see Figure 4). The oxygen content declines approximately 0.04-0.05% (of total weight) from room temperature to 440°C, then increases rapidly by 0.08-0.10% until 455°C. Above 455°C, the oxygen content declines again (see Figure 5). Although the oven was flushed with nitrogen, some residual oxygen in the atmosphere appears to have reacted with the samples when treated in the temperature range 440-455°C.
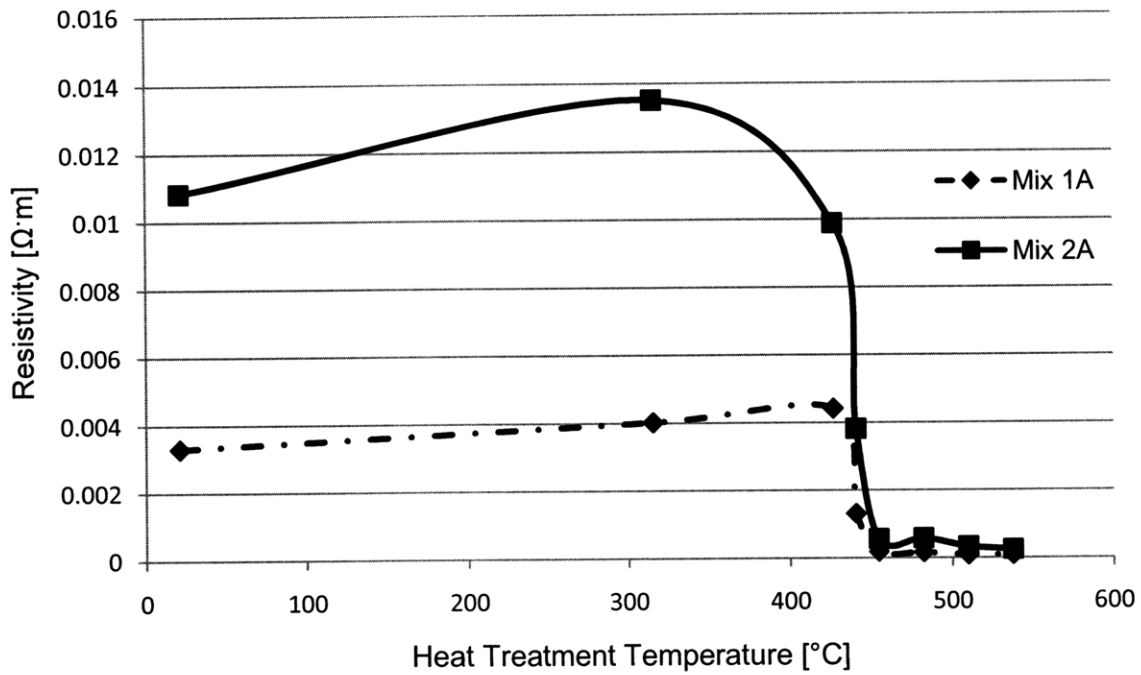
Figure 2. Bulk resistivity of compacted iron powder treated with 0.1%wt and 0.2%wt phosphoric acid (mixes 1A and 2A, respectively), heat-treated in a nitrogen-flushed oven for one hour.
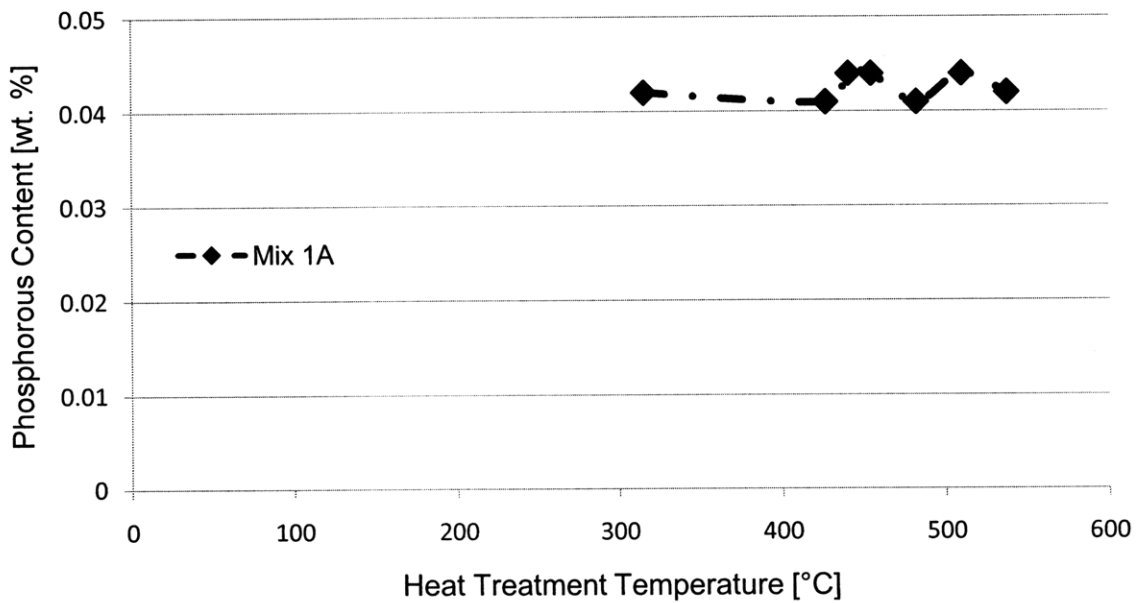

Figure 3. Bulk phosphorus content of compacted iron powder treated with 0.1%wt phosphoric acid (mix 1A) and heat-treated in a nitrogen-flushed oven for one hour.
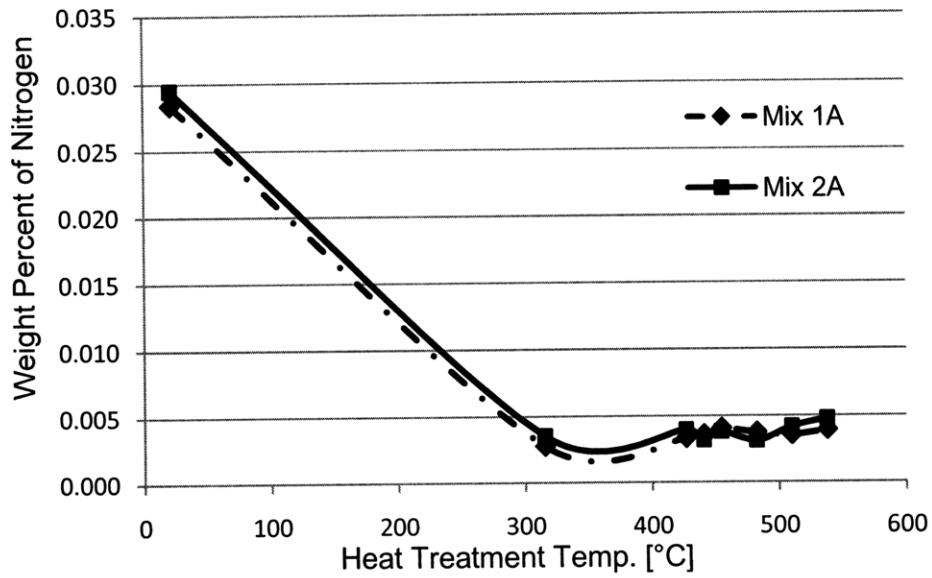
14

Figure 4. Bulk nitrogen content of compacted iron powder reacted with 0.1%wt and 0.2%wt phosphoric acid (Mixes 1A and 2A, respectively) and mixed with 0.75%wt Acrawax lubricant.
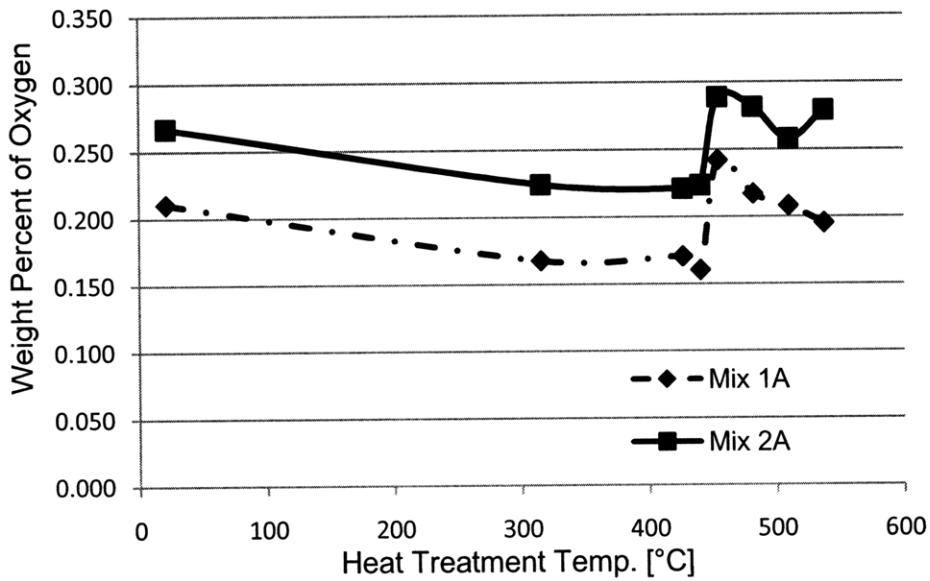

Figure 5. Bulk oxygen content of compacted iron powder reacted with 0.1%wt and 0.2%wt phosphoric acid (Mixes 1A and 2A, respectively) and mixed with 0.75%wt Acrawax lubricant.

SEM Imaging.

Polished samples prepared for the scanning electron microscope (SEM) were observed under an optical microscope. Boundaries between powder particles were easily visible as dark lines between light colored particles. The boundary thickness diminishes with higher temperature heat treatments. The same phenomenon was observed with the SEM, which was also used to analyze the particle interfaces and composition in further detail. The particle boundaries were similarly visible as dark lines, although they could be further resolved and observed to be a gap between particles (Figure 6). Direct particle contact may be relatively sparse, therefore, leading to high contact resistance.

An estimate of the observable gap width between particles may be made by counting the pixel width of the boundaries in SEM images. Multiple measurements were made for each heat-treatment temperature sample to reduce error in measurement. A statistical analysis was made, based on Student's t-test, to illustrate with some certainty that the thinning gap width follows the same trend seen in the resistivity and chemical analyses, namely that the greatest change in gap width occurs in the 425-440°C heat treatment range.
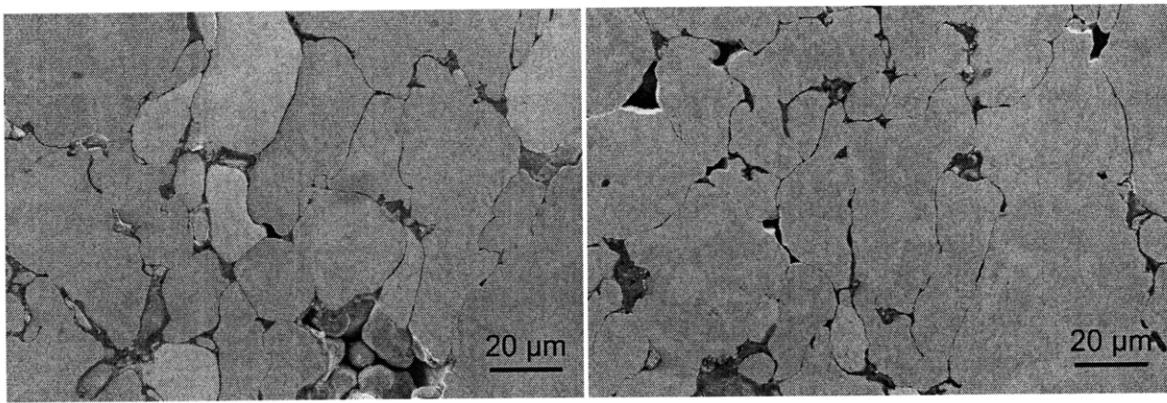
Figure 6. SEM images of cross-sectioned samples of mix 2A heat-treated at (a) 315°C and (b) 440°C. The porosity, as well as the phosphate coating, may influence the electrical resistivity.
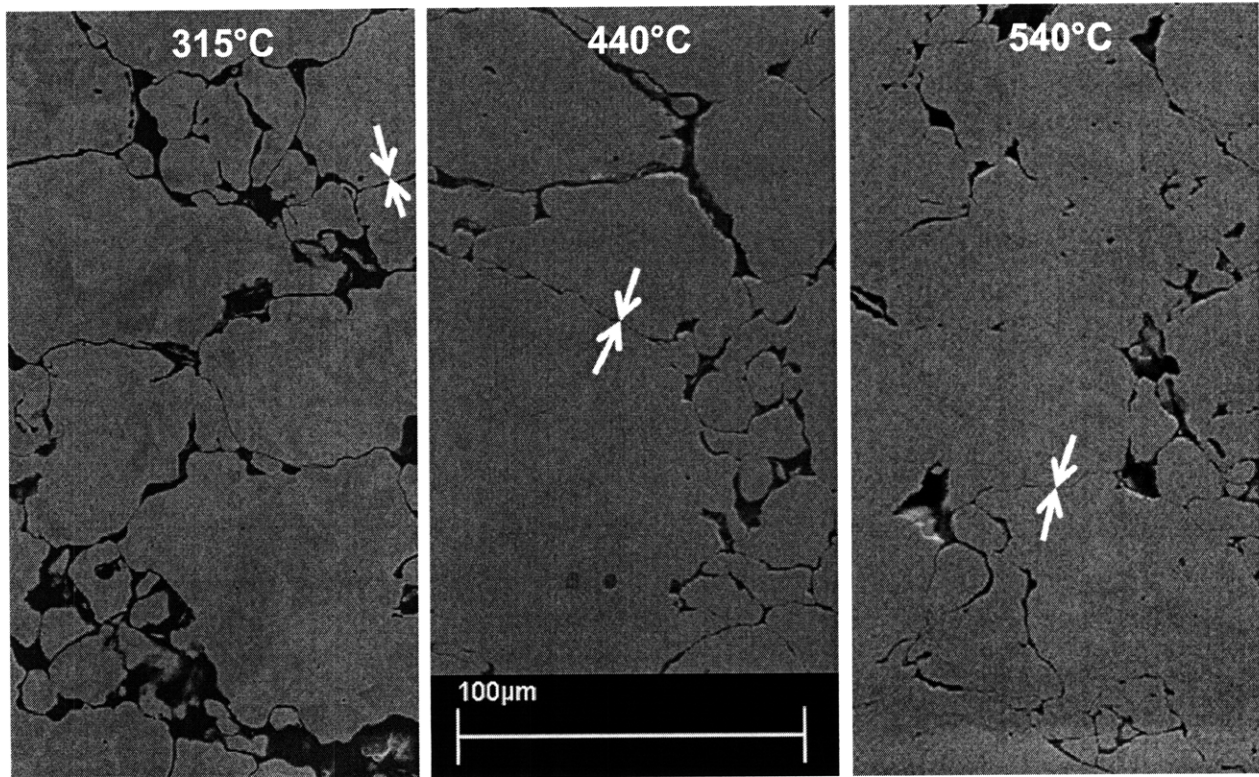

Figure 7. SEM images of compacted mix 2A at several heat treatment temperatures. The average boundary width between individual powder particles may be estimated by counting the pixel width of the boundaries. Several boundary sites were chosen to measure on each sample, one of which is illustrated on each sample in the figure.
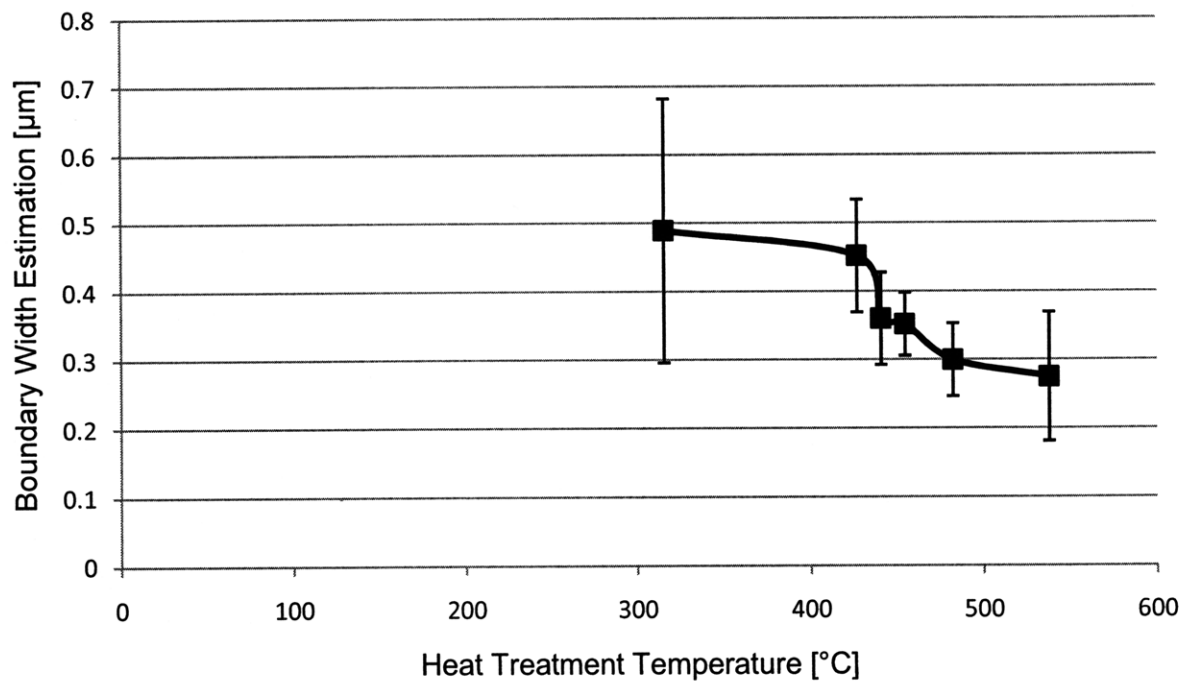
Figure 8. Estimation of boundary width between compacted powder particles of mix 2A versus heat treatment temperature. Estimates were made by counting the pixel width of the boundaries in SEM images. Error bars represent one standard deviation in measurement, derived from Student's t-test.

SEM/EDS Analysis.

The chemistry of the particle boundaries was examined using energy dispersive X-ray spectroscopy (EDS). The count rate of phosphorus was low throughout all samples and approached the limit of the instrument. However, some relatively high phosphorus contents were able to be "seen" within a few micrometers of the particle boundaries, on which the acid treatment is expected to have been localized. The phosphorus did not appear in an even coat on the boundaries; measurable amounts were restricted to few locations along the boundaries. The phosphorus was more readily found and in higher levels in samples treated at lower temperatures. Figures 9, 10, and 11 show EDS linescans across boundaries where phosphorus was detected. If generalized, they indicate that phosphorus appears to diffuse into the powder particles from the boundary at higher temperatures, diminishing the insulating layer on the particle surface. The distance scale in Figure 11 is increased an order of magnitude compared with Figures 9 and 10; the similar profile of the phosphorus curves across all three figures suggest that in Figure 11, the phosphorus has diffused away from the particle surface.
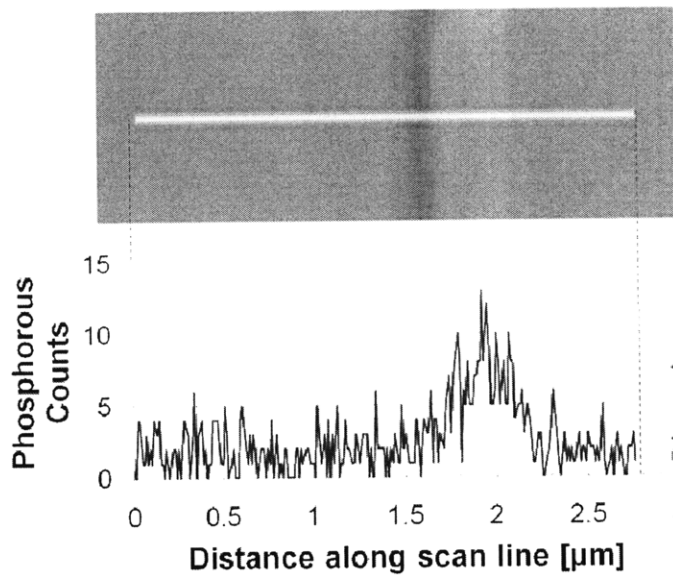
Figure 9. Phosphorus content determined using EDS across a particle-particle interface. The sample is mix 2A heat-treated at 315°C.
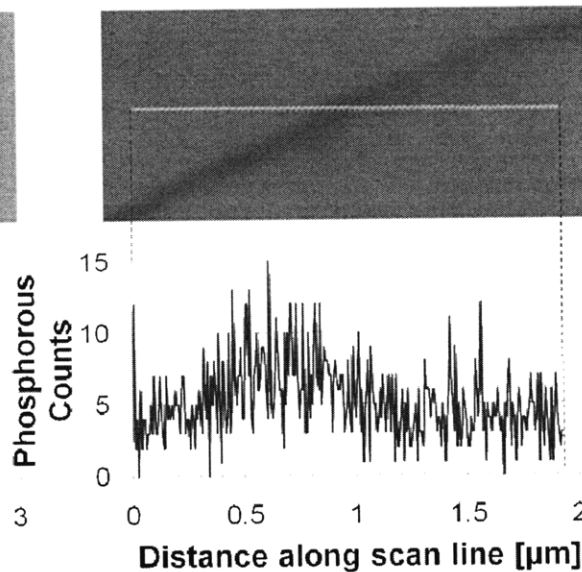

Figure 10. Phosphorus content determined using EDS across a particle-particle interface. The sample is mix 2A heat-treated at 425°C.
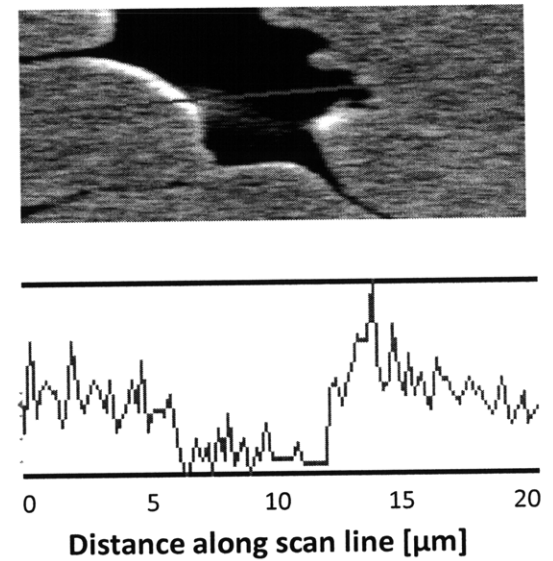

Figure 11. Phosphorus content determined using EDS across a particle-particle interface. The sample is mix 2A heat-treated at 455°C.

TEM Analysis.

Crushed powder of one sample, mix 2A treated at 315°C, was examined under the TEM. Observation of the "dust" made from the sample indicated a microstructure with numerous grains with low-angle boundaries between them. Although possibly a result of the crushing process, this microstructure indicates that a great deal of residual stress exists in 315°C treated samples, which would contribute to the high bulk resistivity of this sample. Without comparable analysis on differently heat-treated samples, no conclusions can be made. Impurities were also seen, but EDS analysis was unavailable to determine their chemistry.

Discussion

With the exception of some oxygen uptake at high temperatures, likely due to inadequate flushing of the oven with nitrogen, the bulk chemistry of the insulated powder does not appear to change with heat-treatment. The changing electromagnetic properties are likely arising from microstructural evolution at high temperatures alone.

The effects of moderate temperature sintering, experienced by the powder in these experiments, likely do affect the electromagnetic properties by reducing porosity. Particle-particle contact area likely is increasing, reducing the contact resistance and bulk resistivity. The relief of cold work through heat treatment is known to reduce the resistivity of the iron substrate. Although this increased resistivity is beneficial to decreasing eddy current losses, the decreased magnetic permeability of iron due to cold work is an impediment to creating a viable PM electromagnetic material. This effect cannot likely be changed in future iron powder-based electromagnetic PM materials.

EDS analysis shows preliminary evidence that phosphorus, localized to particle surfaces when phosphoric acid was reacted with iron powder, is likely diffusing away from the surface. The insulating effects of the iron phosphate surface layer are thereby diminished.

Since the model for eddy current loss largely depends on reducing the size of the domains through which the eddy currents flow (i.e. containing the eddy currents within the powder particles), the effect of reduced particle-particle contact resistance through sintering and phosphorus diffusion is likely the primary cause of reduced electronic quality.

Summary

The results indicate that a number of properties significantly change when heat-treated above 400°C. Heat-treatments above this temperature, required for stress reduction, sintering, increasing magnetic permeability, and decreasing coercivity, have a negative impact on the bulk resistivity. SEM analysis shows that the presence of the phosphate coating at the particle interfaces diminishes with higher temperature heat-treatment. While near the limit of the EDS sensitivity, the phosphorus may be seen to diffuse into the iron particles, reducing the insulating capability of the phosphate coating. The relief of cold work and the process of sintering at high temperatures may also contribute somewhat to the diminishing bulk resistivity. Future work to develop better performing PM materials should look towards developing a coating with reduced potential for diffusion during heat treatment.

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