Effect of Impurities on Aging of Sintered Soft Magnetic Materials

Katie Jo Sunday, Kylan McQuaig
Hoeganaes Corporation
Cinnaminson, NJ 08077

ABSTRACT

Magnetic aging is well known to be troublesome for sintered soft magnetic materials, where magnetic permeability and coercivity worsen over time or when exposed to elevated operating temperatures. Impurities, such as carbon, nitrogen, and oxygen, even in the smallest amounts, lead to large decreases in magnetic performance. This study presents the effects of such impurities on permeability and coercivity with respect to time and temperature to illustrate the importance of process control and avoiding contamination. FF-0000 and FY-4500 materials with various carbon and nitrogen impurity levels are studied to determine absolute magnetic aging effect and potential methods to achieve these results faster in a more controlled manner.

INTRODUCTION

Soft magnetic materials, such as MPIF Standard FF-0000 (pure iron) and FY-4500 (iron with 0.45% phosphorus), are used in a variety of applications including linear actuators, solenoids, and transformer cores.[1] These applications require high magnetic permeability (μ), high magnetic flux density (B), and low coercive force (H_c). To achieve these excellent magnetic properties, impurity levels need to remain low, contamination from other base powders or additives need to be avoided and sintering conditions optimized. Nonmagnetic impurities will reduce magnetic performance overall, however, interstitial impurities (C, O, N) will also reduce structure-sensitive magnetic properties with time. Avoiding contamination with graphite during all stages of production is key to reducing carbon impurities. As graphite is a well-used material in the PM industry, there are various areas where contamination could occur, such as atomizing, blending, compacting, and sintering. Any cross contamination with previous graphite mixes from any step in the process such as mixers, conveyor belts, or sintering trays may cause unwanted carbon pick-up in PM materials. Excess carbon content can also result from improper delubrication and sintering in an endothermic atmosphere that introduces ~20% CO into the furnace.[1] Carbon content should be kept below 0.01%, and ideally below 0.005%, if possible, for the best magnetic performance.[2] Oxygen and nitrogen also need to be avoided, except materials with stable oxides or nitrides, where these atoms cannot move freely from solid solution. Most likely, sintering conditions will affect the amount of unstable oxygen and nitrogen in a sintered material. Not only will these interstitial impurities reduce the magnetic performance of the material after being sintered, but as the materials are aged, they can hurt the magnetic performance substantially more.

If a material ages, the magnetic permeability and coercivity gradually worsen, caused by microstructural changes like impurities precipitating into the lattice. Specifically, carbides and nitrides will interact with magnetic domain walls during the aging process, which leads to slower movement and, therefore, increased coercivity.[2] This results in preferred domain walls where magnetic spins will get pinned during the magnetization process, making the material harder to magnetize, leading to said increase in coercivity. A material is considered nonaging when there is less than 10% increase in coercivity when exposed to an elevated temperature (100ºC) for 200 hours.[4] Even though most applications will not experience these temperatures for extended periods of time, this test method replicates the effect of aging over longer time periods, nominally months and years at normal operating temperatures. Nitrogen absorption in iron is known to degrade properties more when aged at 100 ºC,[5] and has been found to be the active impurity for aging in iron.[6,7] Oxygen affects aging indirectly, by accelerating the precipitation and coalescence of nitrogen and carbon atoms in the form of iron nitrides and carbides, respectively.[4,7] Therefore, the nitrogen content is the primary factor for aging and is mostly driven by the sintering atmosphere, but can also be affected by additive and base iron purity.

This paper studies the effect of carbon and nitrogen content on magnetic properties of FF-0000 and FY-4500. Graphite is admixed to vary carbon content portraying possible contamination, while amount of nitrogen in the sintering atmosphere is also varied. The effect of graphite contamination on magnetic properties is well known, in which carbon amounts greater than even 0.01% will increase coercivity and decrease magnetic permeability. However, some levels of carbon may be unavoidable in the powder metallurgy processes. This study shows not only the effect of carbon on magnetics when initially contaminated, but the detrimental effect when these materials are used for many years after the fact.

We find materials with the lowest carbon content that are sintered in the lowest nitrogen containing atmosphere to show the best magnetic properties when aged. We present the severity of the smallest amount of contamination with nitrogen sintering atmospheres to illustrate the importance of process control for soft magnetic powdered metal components.

EXPERIMENTAL PROCEDURE

Two material systems, FF-0000 and FY-4500, utilize Hoeganaes' Ancorsteel 1000B with 0.75% Acrawax lubricant. FY-4500 materials are produced using Ancorsteel 1000B with 2.9% Fe_3P additive to produce the necessary 0.45% phosphorus content. Graphite was added to mixes to change the amount of carbon in the material, essentially mimicking graphite contamination. Magnetic toroids nominally measuring outer diameter of 32 mm, inner diameter of 22 mm, and height of 6 mm are pressed using uniaxial compaction to a green density of 7.2 g/cm^3 at room temperature. Sintering is performed in an Abbott belt furnace with a preheat zone at 730 ^{o}C and hot zone at 1120 ^{o}C with ~ 20 minutes at temperature. Atmospheres were adjusted according to desired nitrogen content variability from, 90 volume % nitrogen and 10 volume % hydrogen, to 50 volume % of each, to 100 volume % hydrogen. Magnetic testing was performed using an SMT700 hysteresis graph at ~1200 A/m, according to MPIF Standard 35.[8] Samples were tested for DC magnetic properties after sintering, then aged for up to 168 h in air at ~100°C. Some additional studies aged materials at room temperature for extended periods of time, and tested magnetic properties at 4-month intervals.

RESULTS

The negative effect of carbon content on soft magnetic materials is evident in Figure 1, where a graphite addition of 0.05% worsens the as-sintered coercivity and permeability by ~15% for FF-0000 and ~25% for FY-4500, after initial sintering. A much larger increase in coercivity is seen, as to be expected, with graphite additions of greater than 0.1%. Samples in Figure 1 were sintered in 90% N_2 / 10% H_2, tested after sintering, then aged at room temperature, and tested again after 8 months of aging time. FF-0000 and FY-4500 with no graphite additions did not show an aging effect, meaning the difference in coercivity and permeability were very minimal from 0 to 8 months. Percentage values presented in Figure 1, are percent differences from initial sintering to aged for permeability and coercivity. These percentages indicate FF-0000 materials with graphite additions age more than FY-4500 with similar graphite levels. Phosphorus in iron improves the effect of aging by preventing, or at least delaying, the transformation of ε carbides to Fe_3C precipitates.[3] Likewise, aluminum and silicon have been found to inhibit aging by reducing the diffusion rate of nitrogen and carbon in α-iron.[7] In this study, the presence of phosphorus is believed to reduce nitrogen's solubility in iron comparable to silicon and aluminum.[1] As a first assumption, we estimate a material to be non-aging if the coercivity or permeability change is not greater than 10% for the designated testing time. This indicates that all FY-4500 materials, regardless of graphite additions, are non-aging up to 8 months. Although graphite additions may not drastically affect magnetic aging, initial coercivity values are substantially higher than FY-4500 without graphite contamination. As time progresses, coercivity values may also continue to increase and permeability decrease, where these materials no longer meet the non-aging requirements. FF-0000 with ≥ 0.1% graphite addition showed a large change in coercivity from 0 to 8 months, well above the aging limit of 10%. Even with 0.05% graphite, the aging limit is being approached for FF-0000, and with more time values would surpass the 10% limit. These results illustrate the importance of low carbon content and preferable sintering atmospheres, essentially less nitrogen levels.

Time is not always easy to come by during material development, therefore, an accelerated aging method is used. Soft magnetic materials are aged at ~100°C for up to 200 h, and tested for a change in coercivity or permeability. Materials are considered non-aging if the change in coercivity or permeability from as-sintered to aged is less than 10%, known as the aging coefficient, according to the following equation:

$$\frac{\Delta H_c}{H_c} \times 100\% \quad (1)$$

where ΔH_c is the change in coercivity (A/m) from as-sintered to aged, and H_c is the as-sintered coercivity (A/m).[4] The method of aging at an elevated temperature for an extended period is a good indication of the response of the material over long periods of time at room temperature, providing a quantifiable aging measurement for soft magnetic components.

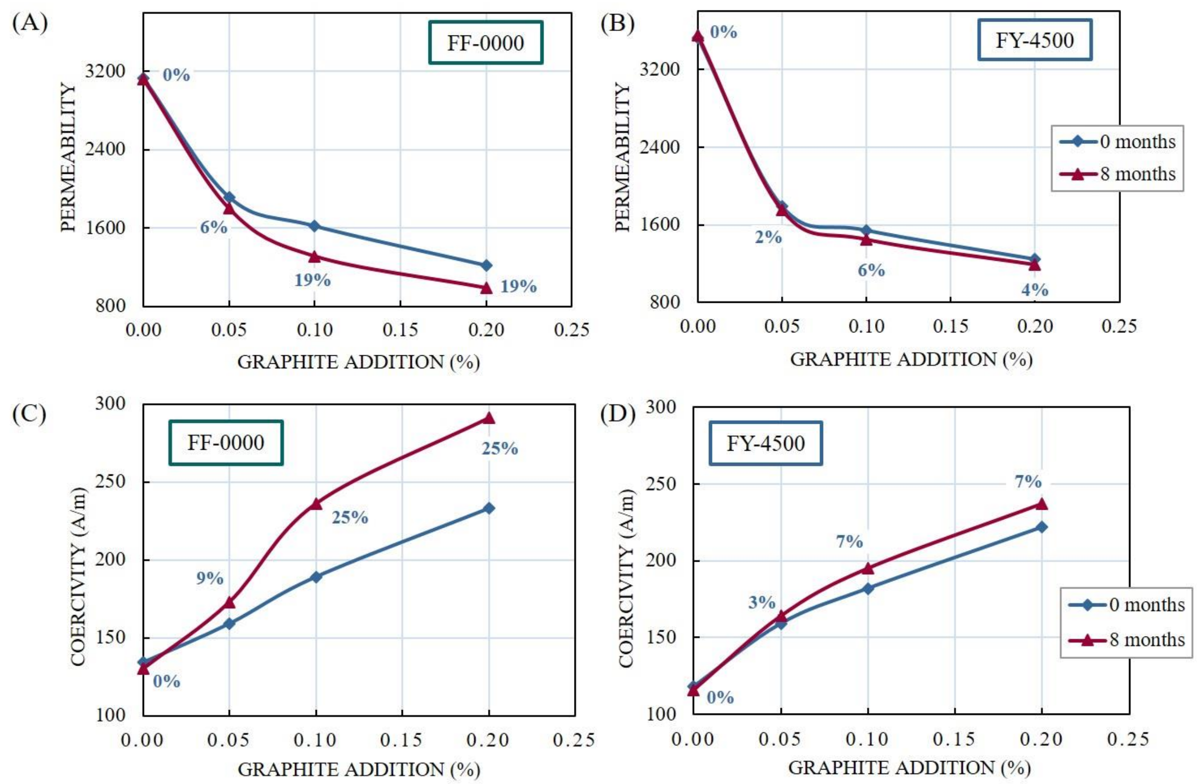

Figure 1: Permeability and coercivity values for FF-0000 and FY-4500, sintered in 90% N_2 / 10% H_2 for increasing graphite additions, aged at room temperature for 8 months. Percentage values displayed on each graph indicate the percent change in coercivity or permeability from 0 months to 8 months.

Mentioned previously, two of the primary factors of aging are nitrogen and carbon content and their precipitation in solid solution as iron nitrides and carbides, respectively.[9] This study shows that the effect of graphite additions coupled with nitrogen pose an even greater threat. More nitrogen is absorbed when more carbon is present in an iron-based powder material, seen in Figure 2, also presented by Hanejko et al.[1] Nitrogen content was varied by adjusting nitrogen volume % in sintering atmospheres, where nitrogen values decreased with increased hydrogen in the atmosphere. For the graphite additions compared in Figure

2, the highest nitrogen content is found with 0.1% graphite addition, sintered in 90% N_2 / 10% H_2. Likewise, a sintering atmosphere of 100% H_2 allowed for very small amounts of nitrogen in all samples, ideal for optimal magnetic performance at the designated sintering temperature. Nitrogen is the primary source for aging and, therefore, should be kept to a minimum in the sintering atmosphere, especially if carbon content is greater than 0.05%, where the two elements heighten the aging effect more.

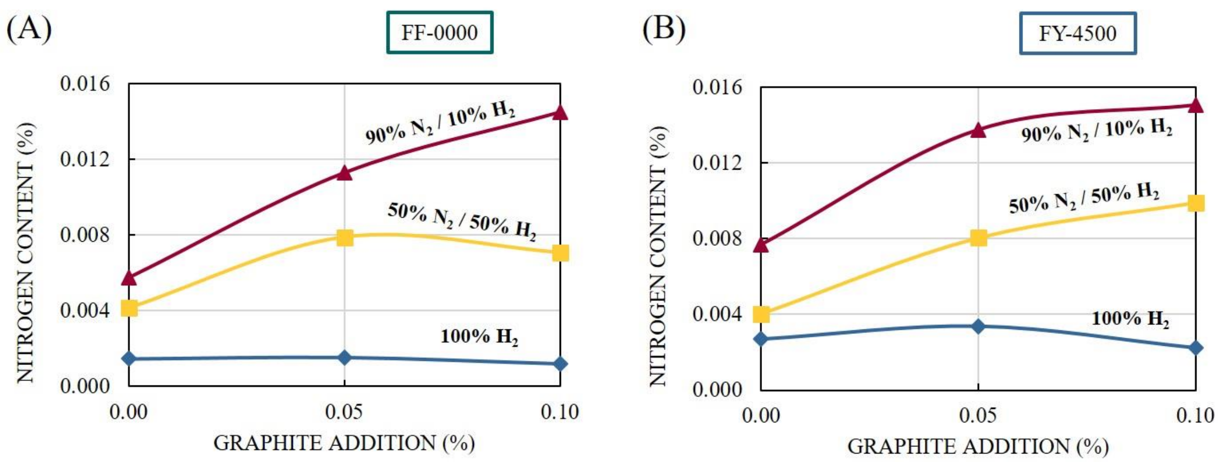

Figure 2: Nitrogen content from as-sintered samples for increasing graphite addition for (A) FF-0000 and (B) FY-4500 materials, illustrating the increase in nitrogen content as carbon content.

Magnetic aging, dependent on nitrogen and carbon content for FY-4500 materials sintered in 90% N_2 / 10% H_2 or 100% H_2, then aged for 168 h at 100°C, is presented in Figure 3 for various graphite additions. Coercivity values for materials with the same graphite content have very similar starting points, regardless of sintering atmosphere. This indicates that the effect of aging may not be seen directly after sintering, but rather, will become evident further on during the life of the part. Even FY-4500 with no graphite contamination will age if sintered in 90% N_2 / 10% H_2. For applications with tight magnetic tolerances, these materials would be unacceptable for long periods of time, and should consider a higher hydrogen content sintering atmosphere to avoid aging effects. All samples sintered in 100% hydrogen, even with graphite additions up to 0.1%, do not show significant increases in coercivity, proving nitrogen is the dominant source for aging in iron-based PM components.

The effect of atmosphere is best described by the aging coefficient, previously explained in Equation 1, where a material is considered non-aging if the coefficient is less than 10% after 200 h at 100°C. Materials sintered in 100% hydrogen are the only materials in this study (aged up to 168 h) to be characterized as non-aging, even with up to 0.1% graphite additions. A sintering atmosphere of 50% N_2 / 50% H_2, for FF-0000 and FY-4500, regardless of graphite additions, had aging coefficients above the 10% limit shown in Figure 4. This study illustrates the importance of sintering atmosphere, where all materials sintered in ≥ 50% N_2 were above the aging limit. If applications do not have a strict magnetic property requirement, then the coercivity increase from aging may be acceptable. However, most soft magnetic applications need coercivity values as low as possible to maintain ideal magnetic performance. For this, sintering should be performed in 100% hydrogen. If a dry hydrogen atmosphere is to be used as this study is suggesting, a proper delubrication step is necessary to minimize excess carbon from remaining after sintering, to improve initial magnetic properties.[1]

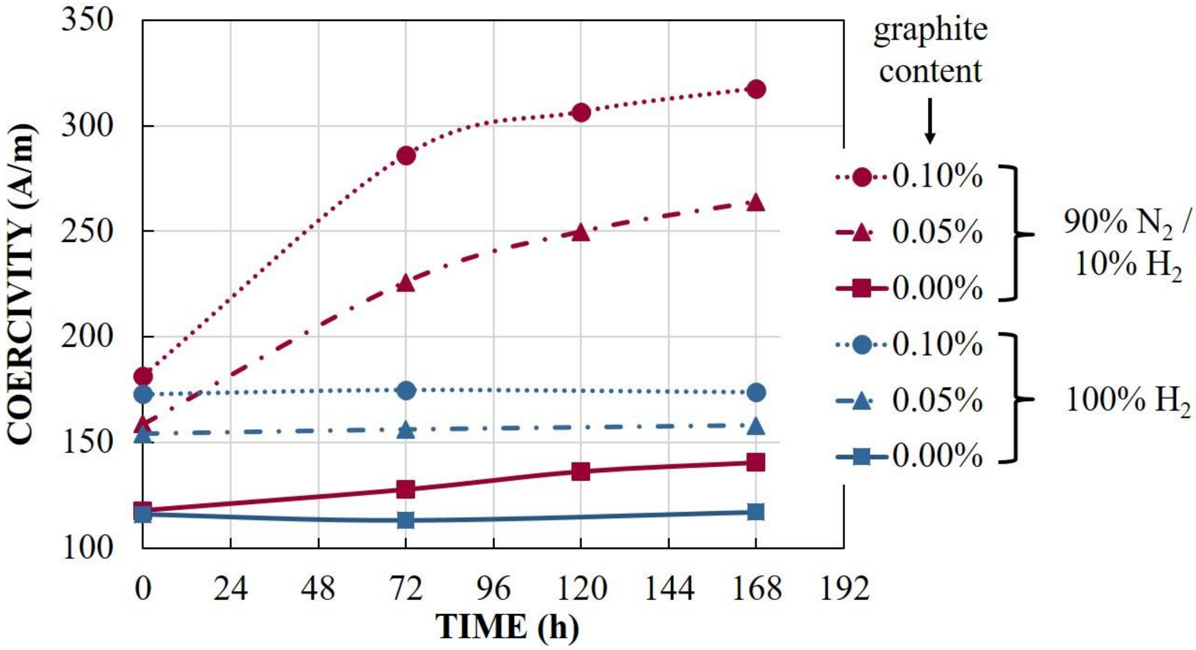

Figure 3: Effect of graphite amount (from 0.0% to 0.1%) and nitrogen atmosphere (from 90% to 0%) on coercivity values for FY-4500 when aged at 100°C, for up to 168 h.

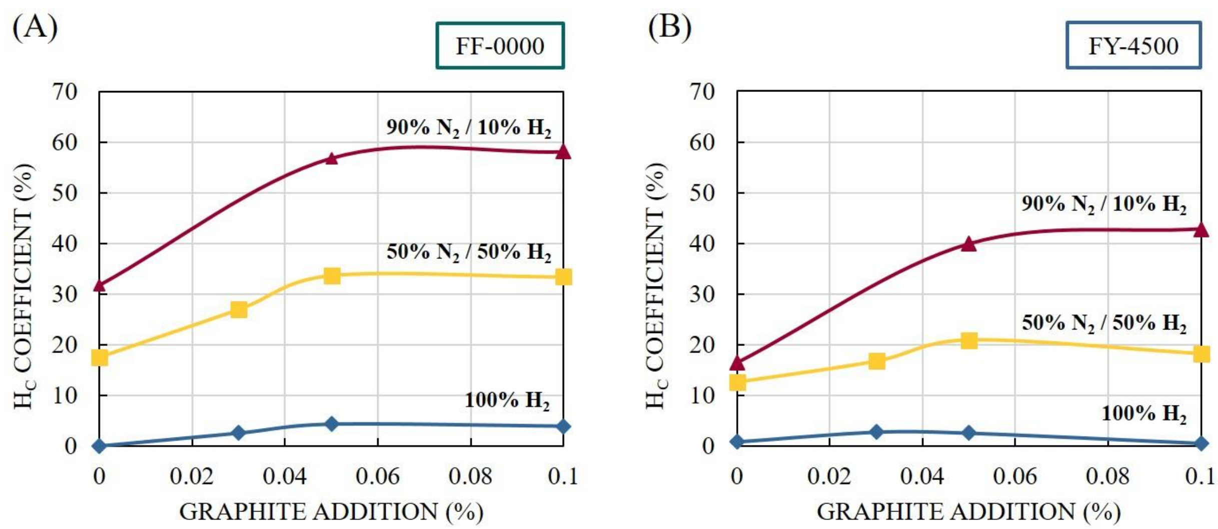

Figure 4: Coercivity (H_c) coefficient calculated after 168h at 100°C, shown for (A) FF-0000 and (B) FY-4500 for graphite addition and sintering atmosphere conditions. Only materials sintered in 100% H_2 are non-aging, H_c coefficient < 10%.

Determination of nitrogen precipitates in FF-0000 and FY-4500 can be difficult to image using light optical microscopy, especially when nitrogen content is below 0.02%. At room temperature, it is known that only 0.008% carbon and 0.006% nitrogen can remain in solution in ferrite. With this, we can explain the increase in H_c coefficient of materials sintered in atmospheres other than 100% hydrogen. Nitrogen amounts greater than the solid solubility level will be free to precipitate through the matrix by forming nonmetallic inclusions. Magnetostatic energy is stored near these inclusions, which can be lowered by domain walls intersecting them and becoming pinned in place.[9] More interruptions in the microstructure results in more energy required during the magnetization process to overcome these regions, leading to higher coercivity and lower permeability. Similarly, carbon levels above 0.008% have a negative effect in terms of forming carbides that precipitate from grain boundaries and further hinder magnetic domain movement by also increasing magnetostatic energy around carbides. This research depicts carbide and nitride precipitates using optical microscopy, shown in Figure 5, for FY-4500 with and without 0.1% graphite additions sintered in 90% N_2 / 10% H_2 or 100% H_2 atmosphere. FY-4500 without graphite showed ferrite microstructure, as to be expected. Sintering in 90% N_2 / 10% H_2 resulted in what is believed to be nitride precipitates from and along grain boundaries, circled in Figure 5B. No such precipitates are found when sintered in 100% hydrogen. Further work will analyze these precipitates in more detail to show their formation and progression during the aging process. FY-4500 with 0.1% graphite addition showed ferrite and some pearlite microstructure with carbide formation along grain boundaries, outlined in Figure 5C. Nitride precipitates were not found from the analysis completed on either FY-4500 with 0.1% graphite, however, future work will continue this research. Potentially, the carbide precipitates mask the nitride precipitates to some extent, therefore Figure 5D does not show any individual nitride precipitates. Since these materials have very small nitrogen contents, it is not surprising that optical micrographs cannot depict nitride precipitates. Carbide precipitates are thin defined regions along grain boundaries that will clearly affect magnetic performance by pinning domain walls, and increasing coercivity. No evidence of nitride formation was found for materials sintered in pure hydrogen, which shows sintering atmosphere controls nitrogen content and therefore nitride precipitates.

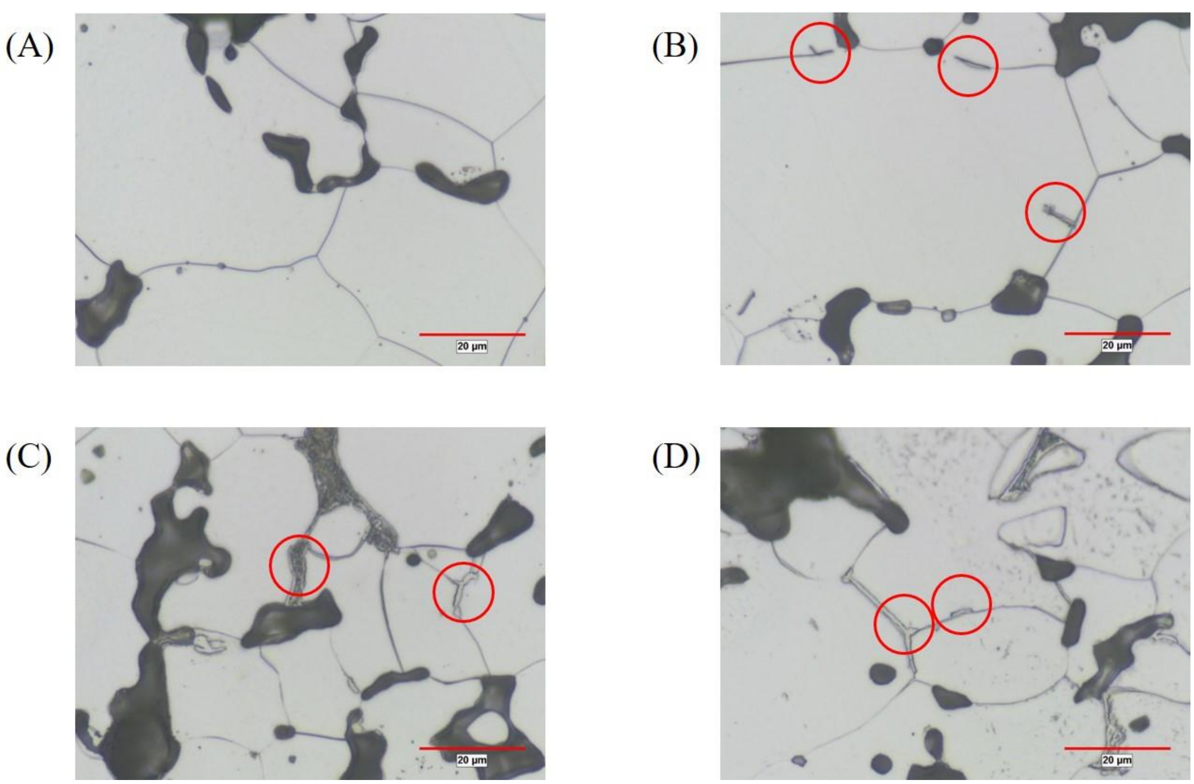

Figure 5: Optical micrographs of FY-4500 with (A and B) 0.0% graphite additions and (C and D) 0.1% graphite additions, sintered in (A and C) 100% H_2 and (B and D) 90% N_2 / 10% H_2.

CONCLUSIONS

Magnetic aging has been shown to greatly reduce magnetic properties of MPIF FF-0000 and FY-4500 powder metallurgy materials. From this study, the following observations have been made:

- Nitrogen absorption during sintering is the leading factor for magnetic aging
- FY-4500 with phosphorus ages less then FF-0000 due to less precipitating of nitrogen
- Effect of atmosphere may only be seen over time or with the accelerated aging method, caution should be taken for nitrogen containing atmospheres for soft magnetic materials
- Higher levels of graphite contamination resulting in higher levels of sintered carbon, accelerate magnetic aging when sintering atmospheres contain nitrogen
- Sintering in pure 100% H_2, even with graphite additions up to 0.1%, remain unaffected by aging
- Avoidance of magnetic aging is only found in a pure 100% hydrogen sintering atmosphere

ACKNOWLEDGEMENTS

The authors wish to thank Todd Nolen for collecting the laboratory data within this manuscript. Tom Murphy and the metallography team of Hoeganaes Corporation for support on micrograph imaging.

REFERENCES

[1] H.G. Rutz, F.G. Hanejko, C.G. Oliver, "Effects of Processing and Materials on Soft Magnetic Performance of Powder Metallurgy Parts", *Advances in Powder Metallurgy and Particulate Materials*, 1992, vol. 6, pp. 375-405, Metal Powder Industries Federation, Princeton, NJ.

[2] C.-W. Chen, *Magnetism and Metallurgy of Soft Magnetic Materials*, 1986, Dover Publications, Inc., New York, NY.

[3] S.K. Ray, S. Mishra, and O.N. Mohanty, "A Study of the Kinetics of Magnetic Aging in Steels", *IEEE Transactions on Magnetics*, 1981, vol. Mag-17, no. 6, pp. 2881-2883.

[4] N.P. Zhetvin, L.N. Podvoiskii, A.I. Paisov, and E.P. Kapustina, "Magnetic Aging of Soft Steel", *Metallovedenie I Term. Obrabotka*, 1960, no. 4, pp. 15-19.

[5] C. Lall, *Soft Magnetism: Fundamentals for Powder Metallurgy and Metal Injection Molding*, 1992, Metal Powder Industries Federation, Princeton, NJ.

[6] R.M. Bozorth, *Ferromagnetism*, 1993, The Institute of Electrical and Electronics Engineers, Inc., New York, NY.

[7] N.M. Benenson, Z.I. Popova, "Kinetics of Magnetic Aging of Low-Carbon Electrical Steel", *Metallovedenie I Term. Obrabotka*, 1968, no. 4, pp. 30-36.

[8] Materials Standards for PM Structural Parts, MPIF Standard 35, 2016 Edition, published by Metal Powder Industries Federation, Princeton, NJ.

[9] M.F. de Campos, M. Emura, and F.J.G. Landgraf, "Consequences of magnetic aging for iron losses in electrical steels", *Journal of Magnetism and Magnetic Materials*, 2006, vol. 304, pp. e593-e595.