Advanced Material Options for High Temperature Sintering

Kylan McQuaig, Alex Wartenberg, Bruce Lindsley, Tom Murphy
Hoeganaes Corporation
Cinnaminson, NJ 08077

Abstract

Materials such as FC-0208 and FN-0205 have been commonly used in the PM industry for many years. These materials offer a good combination of cost and mechanical properties, but they are still limited regarding high-end applications. As raw material prices continue to climb and demand for high strength and ductility parts increases, utilization of next generation materials coupled with high temperature sintering becomes more attractive. Several material options are explored and the potential increase in mechanical properties via high temperature sintering is outlined.

Introduction

The powder metallurgy (PM) industry is constantly evolving and adapting to changing market trends. As vehicle lightweighting becomes more prevalent in the automotive industry and material property demands become more extreme, advanced material options and processing techniques must be developed to meet these needs.

Mechanical properties in PM materials can be increased in several ways, including increasing overall alloy content, raising part density, and/or improving degree of sinter. Increasing alloy content is an attractive option to improve part performance, as it requires little or no change in the subsequent processing operations. But raw material price fluctuation makes this approach riskier than the alternative options. Common PM alloying elements such as molybdenum and nickel have seen substantial price volatility over the past decade [1-3]. Material pricing from the LME Index is shown in Figure 1.

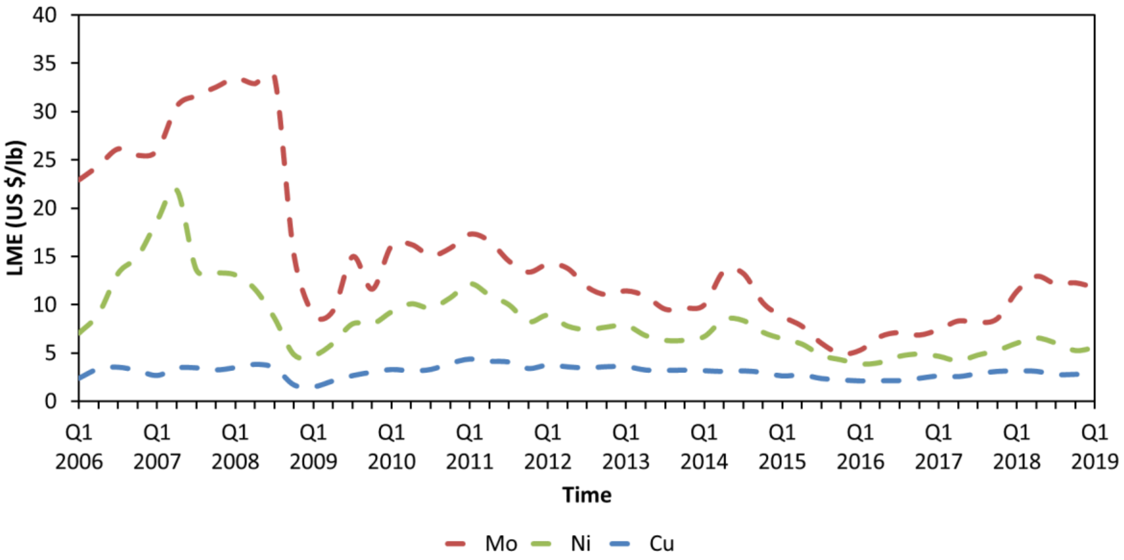

Figure 1: LME Index material costs from 2006-2019 [4].

Compacting parts to higher green density is another viable approach, as this results in comparably processed parts with both higher strength and ductility. Double press double sinter (DPDS) processing has been utilized for many years but necessitates the need for a substantial amount of additional processing. Advanced lubricant options make high density compaction possible in a single step but may require specialized press capabilities as well as potentially higher material cost [5-7].

The use of high temperature sintering is another alternative, allowing for the use of unique alloying elements to achieve similar mechanical properties. With the introduction of improved sintering techniques and through use of high temperature sintering, elements such as manganese, silicon, vanadium, and chromium can be used to replace significantly higher amounts of “standard” PM elements such as nickel and molybdenum [2,3,8-13]. Figure 2 below shows the relationship between oxygen partial pressure and temperature on the stability of some common metal oxides [14]. These alternative alloying elements, which have not been used historically in the PM industry due to their stable oxide formation, become extremely attractive when used in conjunction with high temperature sintering thanks to their effectiveness at relatively low alloy additions.

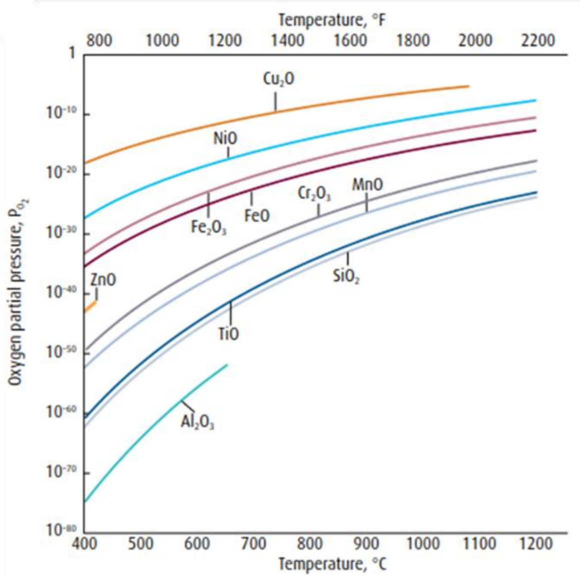

Figure 2: Relationship between oxygen partial pressure and temperature for metal/metal oxide equilibrium [14]

The high temperature sintering approach can be utilized in several different ways, as will be explored in this study. The use of alternative alloying elements presents an opportunity to remove more expensive and highly-regulated alloying elements, such as nickel, from PM alloys [15-16]. Alternatively, mechanical properties can be achieved that are superior to those typically observed in standard PM materials, or leaner alloys can be utilized to drive down material cost while maintaining necessary part performance.

Experimental Procedure

For this study, powder premixes were made using the nominal compositions as shown in Table I. During the first portion of the study, eight “standard” PM compositions were used to determine the benefit of high temperature sintering on common alloys. These compositions are listed by their MPIF standard designation, except for the Ancorsteel^{TM} 4300 material, which does not have a designation and will be referred to by its trade name [17]. The second portion of the study focused on specially designed high temperature sintering (HTS) alloys utilizing alternative alloying elements such as chromium, silicon, and vanadium. All premixes in this study were made using commercially-available water atomized base iron from Hoeganaes Corporation and standard PM alloying additives. All mixes contained 0.75% EBS wax as the lubricant.

Table I: Nominal compositions of premixes explored in this study

MPIF Designation (if applicable)	Fe (%)	Mo (%)	Ni (%)	Cu (%)	Mn (%)	P (%)	Cr (%)	Si (%)	V (%)	C (%)
FY-4500	Bal.	---	---	---	---	0.45	---	---	---	---
F-0005	Bal.	---	---	---	---	---	---	---	---	0.60
FC-0205	Bal.	---	---	2.00	---	---	---	---	---	0.60
FN-0205	Bal.	---	2.00	---	---	---	---	---	---	0.60
FLN2-4405	Bal.	0.85	2.00	---	---	---	---	---	---	0.60
FLNC-4005	Bal.	0.50	1.75	1.50	---	---	---	---	---	0.60
Ancorsteel 4300	Bal.	0.85	1.00	---	---	---	1.00	0.60	---	0.60
FLC2-4808	Bal.	1.25	1.40	2.00	0.40	---	---	---	---	0.60
HTS #1	Bal.	---	---	---	---	---	---	0.75	---	0.90
HTS #2	Bal.	---	---	---	---	---	---	0.60	0.16	0.70
HTS #3	Bal.	---	---	---	---	---	---	0.60	0.16	1.10

All laboratory testing was carried out in accordance with the appropriate MPIF standards [17]. Mechanical properties were measured using transverse rupture (TR), dogbone tensile, and Charpy impact samples compacted to green density of 7.00 g/cm^3 at room temperature. These samples were sintered for approximately 20 minutes at temperature in a mixed atmosphere of nitrogen and hydrogen. Both “normal” and “high temperature” sintering conditions for each mix are shown in Table II. Green and sintered density, apparent hardness, and dimensional change were determined on the TR samples using MPIF Standards 42, 43, and 44, respectively. The mechanical properties of each premix were evaluated on sets of five bars for each test performed.

Table II: Sintering parameters used for each premix in this study

Mix Type	“Normal” Sintering Temperature (°C)	“High” Sintering Temperature (°C)	Atmosphere (N_2%-H_2%)	Approximate Cooling Rate (°C/s)	Tempering Temperature (°C)
FY-4500	1120	1260	0-100	0.7	---
F-0005	1120	1260	90-10	0.7	---
FC-0205	1120	1260	90-10	0.7	---
FN-0205	1120	1260	90-10	0.7	---
FLN2-4405	1120	1260	90-10	0.7	---
FLNC-4005	1120	1260	90-10	0.7	---
Ancorsteel 4300	1180	1260	90-10	1.6	200
FLC2-4808	1120	1260	90-10	1.6	200
HTS #1	---	1260	90-10	0.7	---
HTS #2	---	1260	90-10	0.7	---
HTS #3	---	1260	90-10	0.7	---

Results

All measured mechanical properties in this study are summarized in Table III. All eight standard PM material grades were tested both in a "standard" sintering condition (1120 °C except for the Ancorsteel 4300 material) as well as a high temperature condition of 1260 °C. The HTS alloys are expected to be most effective at high temperature and were, therefore, only sintered at 1260 °C due to the unique alloying elements utilized. As expected, all materials in this study saw increases (to varying degrees) in strength, hardness, elongation, and impact energy following high temperature sintering.

Table III: Summary of mechanical properties of all 11 mixes studied

Mix Type	Sintering Temperature (°C)	TRS (MPa)	Apparent Hardness (HRA)	UTS (MPa)	Elongation (%)	Impact Energy (J)
FY-4500	1120 1260	1034 1525	35 37	353 373	12.7 16.7	45 81
F-0005	1120 1260	634 710	35 36	310 354	3.8 5.2	14 20
FC-0205	1120 1260	965 1000	48 49	503 520	2.7 2.8	15 16
FN-0205	1120 1260	800 883	42 43	401 459	3.5 4.7	19 23
FLN2-4405	1120 1260	1138 1255	55 55	606 663	1.6 2.4	15 19
FLNC-4005	1120 1260	1276 1317	57 57	667 715	2.0 2.3	18 19
Ancorsteel 4300	1180 1260	1779 2151	69 70	1009 1278	1.1 1.8	16 23
FLC2-4808	1120 1260	1662 1779	67 67	946 1063	1.1 1.5	14 18
HTS #1	1260	1220	52	652	3.8	23
HTS #2	1260	1173	54	529	2.3	20
HTS #3	1260	1502	60	738	1.8	18

Focusing on the FY-4500 material, sintered in 100% hydrogen, a substantial increase in mechanical properties is observed. TRS increases nearly 50% and impact energy increases by 80% following high temperature sintering. The accompanying etched microstructures for this alloy can be seen in Figures 3A and 3B. High temperature sintering this material results in a significant amount of pore-rounding and a much larger ferrite grain size. For phosphoruscontaining materials such as FY-4500, contamination prevention and sintering with a higher hydrogen content are vital, as carbon, oxygen, and nitrogen are all known to be detrimental to both mechanical and soft magnetic properties of the sintered components [18].

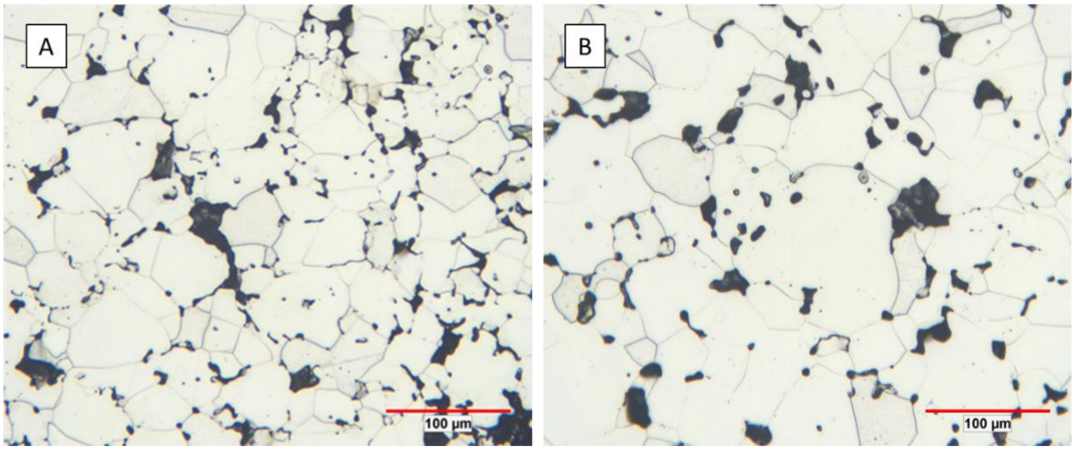

Figure 3: Etched microstructures for FY-4500 sintered at 1120 °C (A) and 1260 °C (B)

For other common PM materials, the increase in mechanical properties with high temperature sintering is not nearly as pronounced. An increase in both TR strength and ultimate tensile strength was observed in each material, but none of the eight "standard" materials outside of FY-4500 and Ancorsteel 4300 experienced a strength increase greater than 15%. Even though strength only increased marginally for many common PM materials, there was a notable increase in both elongation and impact energy for F-0005, FN-0205, and FLN2-4405, specifically. Meanwhile, the two premixes containing admixed copper, FC-0205 and FLNC-4005, saw only minor improvements in properties across the entire temperature range. The etched microstructures of the F-0005, FC-0205, and FLN2-4405 can be seen in Figures 4, 5, and 6, respectively. While the pore rounding is present in all high temperature sintered materials, the microstructural constituents are similar when looking at these three materials, with little difference observed when comparing the two sintering temperatures.

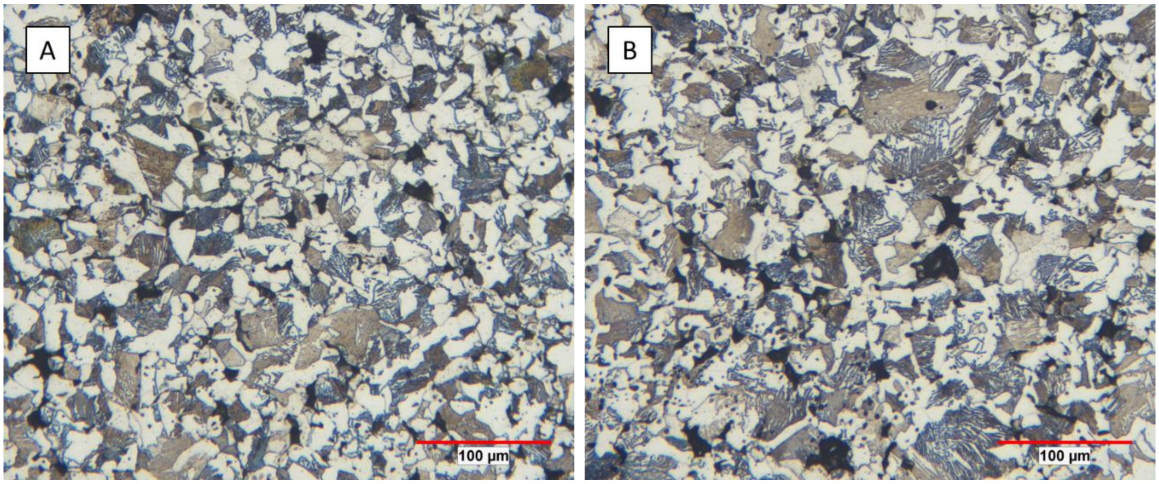

Figure 4: Etched microstructures for F-0005 sintered at 1120 °C (A) and 1260 °C (B)

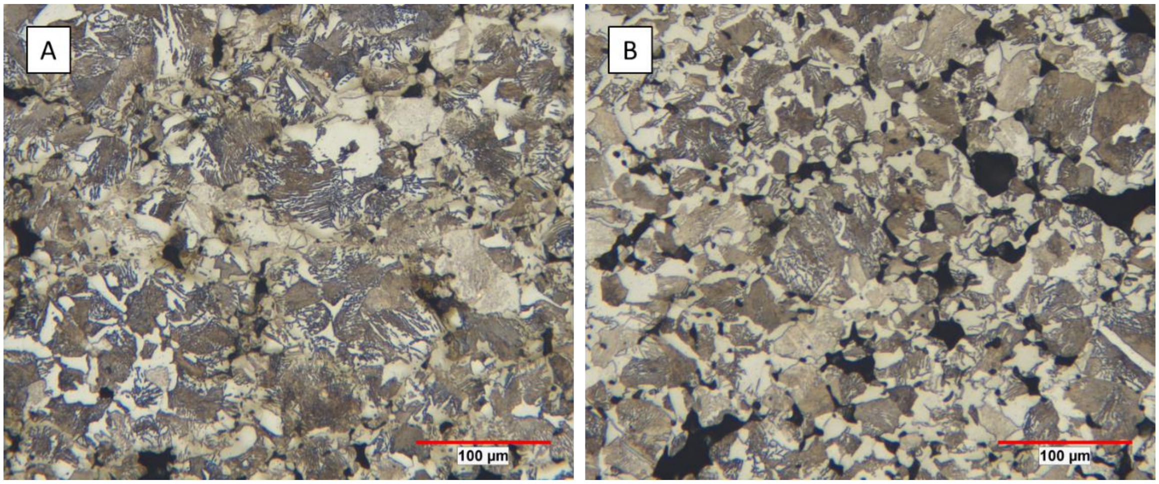

Figure 5: Etched microstructures for FC-0205 sintered at 1120 °C (A) and 1260 °C (B)

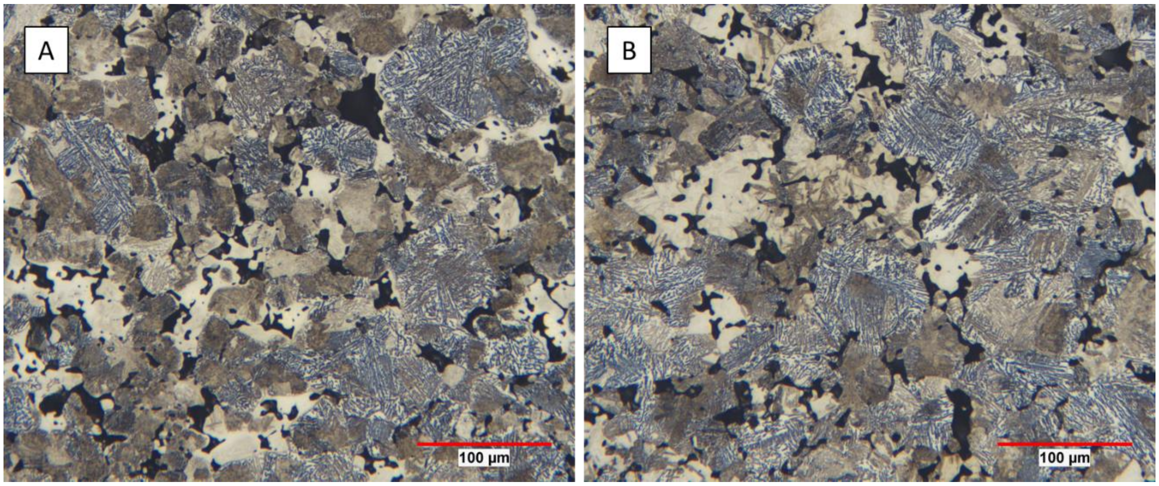

Figure 6: Etched microstructures for FLN2-4405 sintered at 1120 °C (A) and 1260 °C (B)

The next of the “standard” alloys tested was the first sinter-hardening alloy used in this study, Ancorsteel 4300, which contains nickel, chromium, and silicon in addition to the prealloyed molybdenum base iron. This material utilizes some of the same elements as the HTS alloys and, with these alloying elements present, it would be expected to perform very well with high temperature sintering. In fact, the “standard” sintering temperature recommended for this alloy is 1180 °C, which is needed to facilitate the reduction of chromium and silicon oxides to obtain proper diffusion. Even though the high temperature sintering (done at 1260 °C) was done only 80 °C higher than the standard sintering for this material, a drastic improvement in mechanical properties and microstructure can be observed (Figures 7A and 7B). There were dramatic improvements in strength, elongation, and impact due to a more uniform diffusion of the alloying elements. Figure 7A shows the etched microstructure of the sinter-hardened material sintered at 1180 °C, with martensite, large islands of bainite, and a number of nickel-rich areas where the Ni is more highly concentrated. In contrast, Figure 7B has a much higher percentage of martensite and more thorough diffusion of the nickel has taken place.

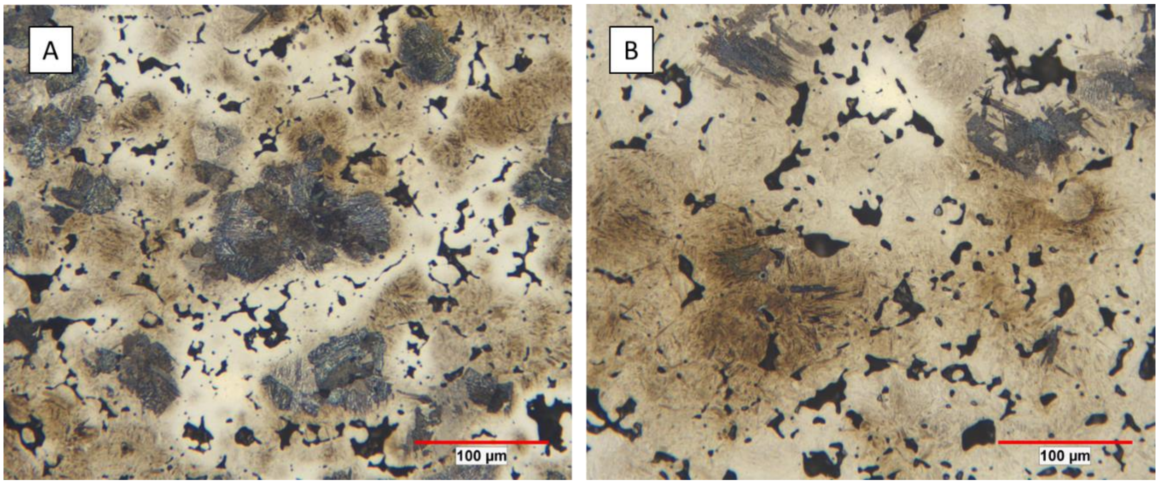

Figure 7: Etched microstructures for Ancorsteel 4300 sintered at 1180 °C (A) and 1260 °C (B)

The same trends did not hold true when high temperature sintering the other sinter-hardening material, FLC2-4808. While the elongation and impact do increase somewhat, there is almost no increase in strength and both sets of samples were found to have a fully martensitic microstructure as shown in Figures 8A and 8B.

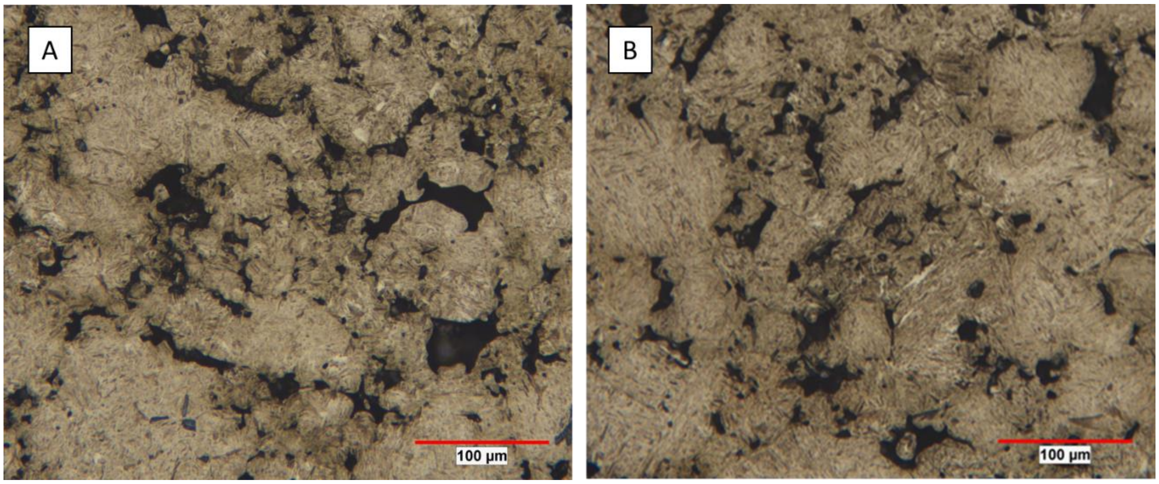

Figure 8: Etched microstructures for FLC2-4808 sintered at 1120 °C (A) and 1260 °C (B)

Similar to the Ancorsteel 4300 material, the HTS alloys reach optimal properties through high temperature sintering. Each material showed a good combination of strength and ductility in the final properties. Figure 9 shows the typical pearlitic microstructure that was observed for each of the HTS alloys. As shown in the figure, the lamellar spacing of the pearlite is extremely fine. The presence of silicon and vanadium in these alloys strengthens and refines the microstructure, while also preventing the formation of carbides, even with the 1.1% graphite addition in HTS #3.

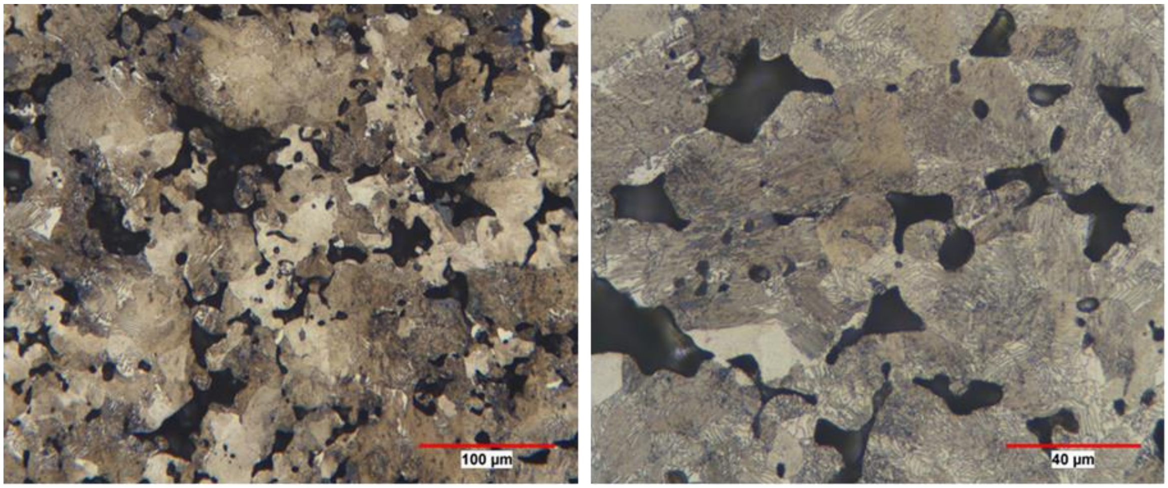

Figure 9: Etched microstructure at two magnifications for HTS #1 sintered at 1260 °C

Discussion:

Regarding the standard PM alloys, the largest improvements were in elongation and impact energy following high temperature sintering. Table IV shows the percent increase in each property for a given material type when increasing sintering temperature from the "standard" to 1260 °C. Most materials had approximately 10% increase in TRS and UTS, 30-50% increase in elongation, and 20-50% increase in impact. For FY-4500, the improvements in TRS and impact were far more dramatic. There was also a more pronounced benefit in elongation and impact energy with the materials containing admixed nickel, such as the FN-0205 and FLN2-4405. Meanwhile, the materials with admixed copper showed very little improvement in mechanical properties. Copper is utilized in powder metallurgy because it melts at standard sintering temperatures, allowing for more rapid liquid-phase sintering and strengthening of the particle necks. For this type of material, clearly high temperature sintering does not provide as great a benefit compared to other common PM alloys.

Table IV: Percentage improvement in property following high temperature sintering

Mix Type	TRS (%)	UTS (%)	Elongation (%)	Impact Energy (%)
FY-4500	47	6	31	82
F-0005	12	14	37	50
FC-0205	4	3	4	9
FN-0205	10	14	34	21
FLN2-4405	10	9	50	27
FLNC-4005	3	7	15	8
Ancorsteel 4300	21	27	64	42
FLC2-4808	7	12	36	30

To highlight the mechanical properties achievable with the HTS alloys, Table V shows UTS and impact energy as well as total alloy content, compared with selected standard alloy systems. The two standard alloys chosen, FLN2-4405 and FLNC-4005, would be considered "high-end" materials in the PM industry in terms of alloy content, material properties, and cost. Both materials use a prealloyed molybdenum base iron and admixed nickel, with total alloy content in the 3-5% range. The HTS alloys, each utilizing an unalloyed iron base and less than 2% total alloy content can essentially match both strength and ductility of these alloys when used in conjunction with high temperature sintering. If even higher properties are desired, a prealloyed base iron can be used with these same additive amounts, similar to what is observed with the Ancorsteel 4300 material, which far exceeds the mechanical properties shown in Table V.

Table V: Properties achieved at 1260 °C for select mixes compared to total alloy content

Mix Type	UTS (MPa)	Impact Energy (J)	Total Alloy (%)
FLN2-4405	663	19	3.45
FLNC-4005	715	19	4.35
HTS #1	652	23	1.65
HTS #2	529	20	1.46
HTS #3	738	18	1.86

Conclusions

As a result of the experimental work performed during this study, the following observations were made:

- High temperature sintering increases the strength (TRS and UTS), elongation, and impact energy of all alloys tested in this study as a result of pore round and improved degree of sinter.
- Certain properties, such as elongation and impact energy, improved dramatically in most materials, while strength was more material-dependent. In applications where maximizing material ductility is desired, high temperature sintering is most beneficial.
- In FY-4500 and premixes with admixed nickel, there was a substantial improvement in static mechanical properties as a result of high temperature sintering. Materials containing admixed copper saw only a marginal improvement as a result of high temperature sintering.
- Silicon and vanadium were effective at refining material microstructure and preventing carbide formation, even at high graphite additions.
- Alloying elements such as Cr, Si, and V can be utilized to achieve properties equivalent to more highly alloyed PM materials, providing a route for leaner materials and cost savings through improved processing. The elements may also provide a route to nickel-free alloys if desired.

Acknowledgements

The authors want to thank Meghan Fields, Jeanne Falzone, Eric Alesczyk, and Barry Diamond for all their contributions to this manuscript.

References

1. *Nickel price soars amid export ban and sanction fear,* Powder Metallurgy Review, (2014), Vol. 3, No. 2, p. 10.
2. B. Lindsley, *High performance manganese containing PM steels,* Advances in Powder Metallurgy & Particulate Materials, compiled by R. Lawcock, A. Lawley and P. J. McGeehan, MPIF, Princeton, NJ, (2008), part 7, p. 17-25.
3. B. Lindsley, W.B. James, *PM steels that contain Mn,* Advances in Powder Metallurgy & Particulate Materials, compiled M. Bulger and B. Stebick, Metal Powder Industries Federation, Princeton, NJ, (2010), part 10, p. 36-49.
4. London Metal Exchange, (2019), Online, Available: https://www.lme.com/Metals.
5. H. Rutz, F. Hanejko, *High Density Processing of High Performance Ferrous Materials*, Advances in Powder Metallurgy & Particulate Materials – 1994, compiled by C. Lall and A. Neupaver, Metal Powder Industries Federation, Princeton, NJ, 1994, Vol. 5, pp. 117-133.
6. F. Hanejko, *Warm Die Compaction with Reduced Lubricant Levels Promoting Higher Green and Sintered Densities,* APMA 3rd International Conference on Powder Metallurgy, Kyoto, Japan, (2015).
7. A. Wartenberg, C. Schade, *Double Press Double Sinter Alternatives for High Density Applications*, Advances in Powder Metallurgy & Particulate Materials, Vol. 1, p. 266-275, (2017).
8. P. King, *Chromium Containing Materials for High Strength – High Fatigue Applications,* PM World Congress Proceedings (2004).
9. C. Schade, T. Murphy, A. Lawley, R. Doherty, *Microstructure and Mechanical Properties of PM Steels Alloyed with Silicon and Vanadium,* International Journal of Powder Metallurgy, (2012), 48/6, p. 41-48.
10. B. Lindsley, C. Schade, T. Murphy, *Vanadium and Silicon Alloyed PM Steels*, Euro PM Congress Proceedings (2013).
11. C. Schade, T. Murphy, A. Lawley, and R. Doherty, *The Influence of Silicon on the Mechanical Properties and Hardenability of PM Steels*, Advances in Powder Metallurgy and Particulate Materials, (2013), compiled by D. Christopherson and R.M. Gasior, MPIF, NJ, vol. 7, pp. 54-72.
12. C. Schade, T. Murphy, , A. Lawley, R. Doherty, *Microstructure and Mechanical Properties of a Bainitic Powder Metallurgy Steel,* International Journal of Powder Metallurgy, (2016), Vol. 52, No. 2, p37-46.
13. D. Milligan, U. Engstrom, S. Smith, *High Temperature Sintering – a Cost Effective Way to Future High Performance Materials*, PM^{2}TEC2005 Proceedings, Montreal, Canada, (2005).
14. *Furnace atmospheres no. 6: Sintering of steels,* The Linde Group.
15. B. Neumann, G. Kotthoff, V. Arnhold, *REACH: Risks, challenges and opportunities for sintered parts manufacturers,* published in Pulvermetallrugie in Wissenschaft und Praxis, Vol. 28, (2012).
16. J. Khambekar, B. Pittenger, *Understanding and Preventing Metal-Dust Hazards,* International Journal of Powder Metallurgy, Vol. 49, Issue 4, (2013).

17. Standard Test Methods for Metal Powders and Powder Metallurgy, Metal Powder Industries Federation, Princeton, NJ, 2016 Edition.
18. K. Sunday, K. McQuaig, *Effect of Impurities on Aging of Sintered Soft Magnetic Materials*, Presented at: PowderMet 2018, San Antonio Texas, (2018).