A Study Comparing the Performance of Natural Flake Graphite from Two Different Geographical Regions in PM Alloys F-0008, FC-0208, and FN-0208

Albert V. Tamashausky
Director of Technical Services
Asbury Graphite Mills Inc.
albert@asbury.com
March 19, 2018

Abstract: A study to determine the effect of commutated graphite from different geographical origins on the properties of three different Powder Metallurgy (PM) alloys was performed. Graphite alloy powders representing two different particle size specifications were manufactured and used at addition rates specified by the standardized alloy composition. Powder, green-compact and sintered properties were measured. Test bars used for green and sintered testing were pressed 30, 40, and 50 KSI. Testing included Hall flow and density, green density, green strength, green dimensional change from die, sintered density, sintered TRS, sintered apparent hardness, and dimensional change. Metallographic images of each microstructure were prepared and characterized. Test results indicate that there is no difference in either green or sintered properties, for all compact pressures, resulting from the use of graphite from the different origins used in this study. Metallographic images are typical and unremarkable.

Introduction:

Asbury Carbons Inc is the world's largest manufacturer and supplier of commutated natural flake graphite-based alloy carbons to the PM industry. Natural flake graphite of nominal 95% graphite content is used routinely as a source of carbon for PM alloys that require carbon addition. Properly commutated and size-classified natural flake graphite powders exhibit complete solution/diffusion into PM matrices and the resulting alloys have historically exhibited exceptional homogeneity and physical properties.

Since the 1990s, Asbury Carbons' primary natural graphite feed stock for "PM" grades has been limited to flake sourced from locations primarily in mainland China, with minor amounts originating from Canada. It is the opinion of Asbury Carbons that as new applications and demands for graphite materials develop; demand evolution will negatively disrupt the established Chinese supply chain for international markets. An example of an application that may utilize large quantities of natural flake graphite is lithium ion battery technology.

In order to strategically address anticipated supply chain tightening, qualification of alternative global supply base geographies for the supply of natural flake graphite is critical for the PM industry. The purpose of this research is to determine the utility of a non-Chinese flake graphite source as a PM alloy carbon material, with the goal of diversifying the range of natural graphite sources acceptable in PM applications.

Methods and Materials:

Two different natural flake graphite materials, one originating from an ore body located in Madagascar, and one originating from an ore body located in China, were processed using identical milling technology. Two different products were manufactured from each graphite "type". One product conformed to Asbury specification 3203, a nominal 5µm powder. The second product conformed to Asbury specification 1651, a nominal 10 µm powder. Both of these product specifications apply to grades manufactured exclusively for PM alloy applications and are well known industry "standards".

Each of the graphite types described above was assayed and fully characterized. Testing included chemical and physical analysis, particle size distribution, determination of morphology, and XRD crystallographic profile. These data, with brief commentary, are presented below.

Table 1: Chemical profile

Grade/Product/Specification	3203	3203	1651	1651
Asbury Lot Number	19924	22674	21316	22675
Origin	China	Madagascar	China	Madagascar
Carbon (%)	96.42	95.61	95.99	95.53
Volatile (%)	1.06	2.02	1.09	1.32
Moisture (%)	0.13	0.15	0.09	0.08
Sulfur (%)	0.173	0.006	0.226	0.011

Except for the lower sulfur content in the Madagascar flake, the gross chemical profiles of these materials are similar and unremarkable. In natural graphite free sulfur is not present: Sulfur is present in combined form in minerals such as gypsum, anhydrite, pyrite, etc.

Table 2: Trace Element Analysis:

Grade/Product/Specification	3203	3203	1651	1651
Asbury Lot Number	19924	22674	21316	22675
Origin	China	Madagascar	China	Madagascar
(1) Ash Oxide (%)				
Al2O3	15.57	39.4	14.47	38.12
BaO	0.08	0.03	0.07	0.03
CaO	3.87	0.24	4.58	0.48
CoO	0.01	0.00	0.01	0
Cr2O3	0.03	0.03	0.03	0.03
CuO	0.16	0.06	0.19	0.11
Fe23O3	15.09	5.12	15.65	5.05
K2O	5.21	3.40	4.58	3.4
MgO	5.70	0.39	5.01	0.48
MnO2	0.22	0.04	0.24	0.03
MoO3	0.33	0.03	0.37	0.02
Na2O	0.20	0.15	0.17	0.19
NiO	0.05	0.05	0.07	0.04
SiO2	52.77	50.78	53.66	51.76
TiO2	0.48	0.10	0.55	0.13
V2O5	0.2	0.12	0.29	0.08
ZnO	0.05	0.05	0.05	0.05

The total ash content of the two sources is similar and both products are characterized as nominal 95% minimum carbon flake. Although the total calculated silicon dioxide content is similar for both origins, there is a shift in the calculated aluminum, iron, magnesium, and calcium oxide content.

The calculated alumina content for the Chinese origin flake is approximately 15%, in contrast to 39% for the Madagascar flake. The iron oxide content, 15% in the Chinese origin flake, drops to 5% in the Madagascar product. In the Chinese flake the calculated magnesium oxide content is approximately 5%, but is under 0.5% in the Madagascar material. A similar trend is indicated in the calcium oxide content which is present at about 4% in the Chinese flake but less than 0.5% in the Madagascar flake.

Note the values in Table 2, in which elemental components are expressed as oxides, are calculated values. Most of the oxides listed are not components associated with the graphite ash. These calculated oxides are based on ICP assay, during which the mineralogical integrity of the sample is obliterated. The non-carbonaceous minerals associated with natural graphite are complex oxide, silicate, and aluminosilicate mineral phases. In general the only pure oxides, which may be present in limited quantities, are silicon dioxide (quartz), and iron oxide (hematite or magnetite).

Table 3: Laser particle size profile

Grade/Product/Specification	3203	3203	1651	1651
Asbury Lot Number	19924	22674	21316	22675
Origin	China	Madagascar	China	Madagascar
MTRAC (Summary Data)				
MT%10	2.20	2.24	4.13	3.7
MT%50	5.10	5.22	9.49	8.99
MT%90	9.21	9.6	17.76	18.28
MTMV	5.52	5.69	10.59	10.38
MTSTD	2.67	2.86	5.18	5.43

Laser particle size profiles are unremarkable and indicate that each of the powders conform to the associated grade's particle size specification.

Table 4: Physical property values

Grade/Product/Specification	3203	3203	1651	1651
Asbury Lot Number	19924	22674	21316	22675
Origin	China	Madagascan	China	Madagascan
Surface Area (m^2/g)	11.5	12.3	8.1	8.5
Wetability (Yes / No)	Yes	No	No	No
True Density (g/cc)	2.27	2.25	2.28	2.30
Press Density (g/cc)				
@6,500 psi	1.79	1.81	1.86	1.89
@32,500 psi	2.17	2.19	2.22	2.25

Physical properties differences between powders made using different origin graphite are unremarkable and any differences observed are attributable to the differences in particle size.

Table 5: XRD Crystallographic Profile

Grade/Product/Specification	3203	3203	1651	1651
Asbury Lot Number	19924	22674	21316	22675
Origin	China	Madagascar	China	Madagascar
XRD Data				
Si, Internal Standard, measured 111 2-theta (Expected 28.4441º)	28.28	28.29	28.36	28.38
Graphite, 002 2-theta, Degrees	26.433	26.451	26.463	26.468
Graphite, 002 d-spacing, Å	3.369	3.367	3.369	3.365

The XRD profiles identify the presence of fully graphitized carbon, and are otherwise unremarkable.

All natural flake graphite materials exhibit flaky or platy morphology. The following figures are SEM micrographs of the four graphite materials evaluated in this study. Each image shows a random field at 2500X magnification.

Figure 1: 3203-Chinese Flake

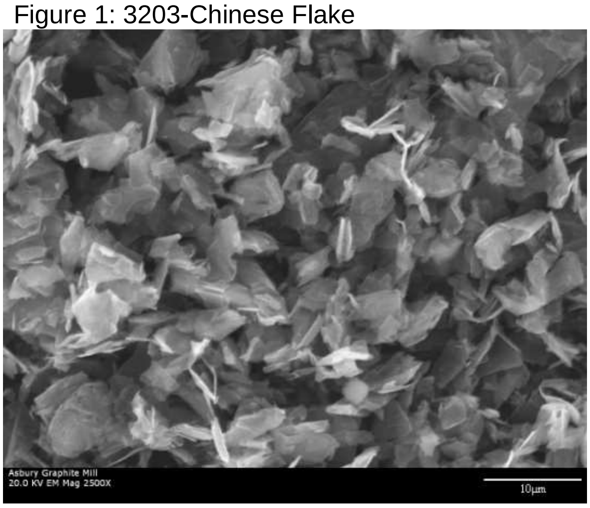


Figure 2: 3203-Madagascar Flake

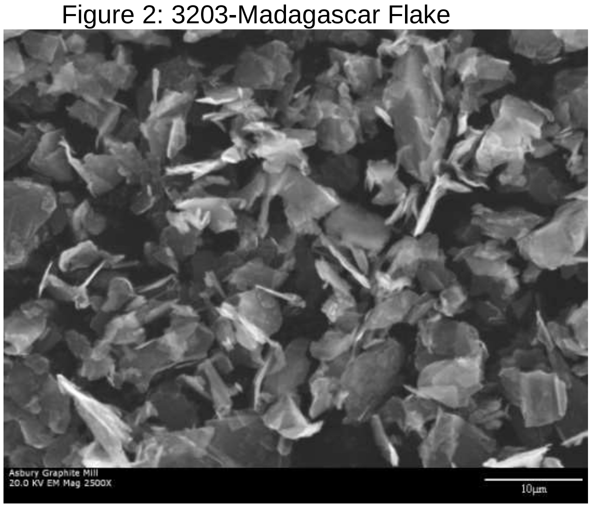


Figure 3: 1651 Chinese Flake

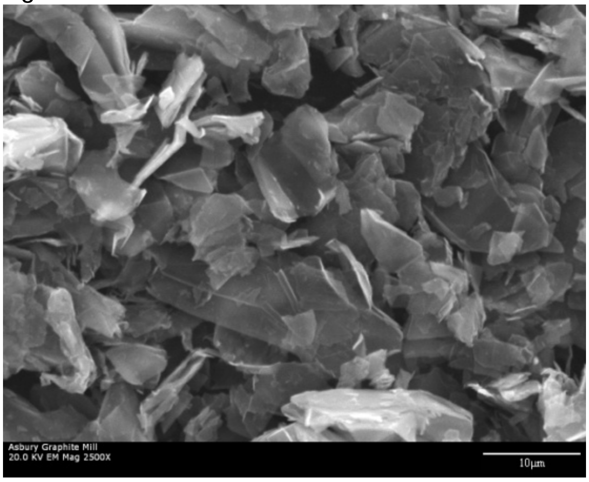
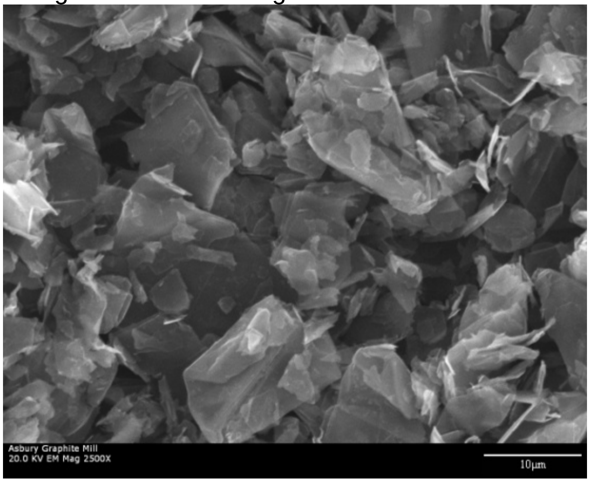


Figure 4: 1651 Madagascar Flake



Figures 1-4 show particles with identical morphology typical of milled natural flake graphite. Particles which appear to be fibers are actually images of $(10\bar{1}0)$ prismatic edges, of graphite flakes, oriented parallel to the viewer's perspective.

Three different standard PM formulations were used in this study: F-0008, FC0208, and FN0208. Each graphite material was used as the carbon alloy additive in each of the PM products, which resulted in a 12 sample matrix. Each mixture was formulated with 0.8% Acrawax-C, added as lubricant. Mixtures were compounded using a laboratory rotary mixer. Glass mixing vessels were used and all mix times were 20 minutes. Mixture homogeneity was verified for each trial. Table 6 presents the formulations for each mixture.

Table 6: Mixture formulations

Mix#	MPIF Grade	Iron, % A1000B "1"	Copper% 8081 "2"	Nickel % 123 "3"	AcrawaxC Wt %	3203 China "A"	3203 Madagascar "B"	1651 China "C"	1651 Madagascar "D"
1A *	F0008	98.4			0.8	0.8			
2A	FC0208	96.4	2.0		0.8	0.8			
3A	FN0208	96.4		2.0	0.8	0.8			
1B	F0008	98.4			0.8		0.8		
2B	FC0208	96.4	2.0		0.8		0.8		
3B	FN0208	96.4		2.0	0.8		0.8		
1C	F0008	98.4			0.8			0.8	
2C	FC0208	96.4	2.0		0.8			0.8	
3C	FN0208	96.4		2.0	0.8			0.8	
1D	F0008	98.4			0.8				0.8
2D	FC0208	96.4	2.0		0.8				0.8
3D	FN0208	96.4		2.0	0.8				0.8

*Note that going forward in this paper; samples are identified by the number of the metal powder followed by the letter designation of the graphite powder.

Results: Green and sintered properties were measured on each of the twelve mixtures prepared for this study. Green powder samples were tested for both Hall Apparent Density and Hall Flow Rate. Test bars were prepared from each mixture by compaction at 30TSI, 40TSI, and 50TSI. Green property measurements included Green Density, Green Strength, and % Green Spring from Die Size. Sintered properties were measured and include Sintered Density, Transverse Rupture Strength, Apparent Hardness, and % Dimensional Change from Die size. Reported green and sintered values are the average of test data taken on three test bars for each property reported.

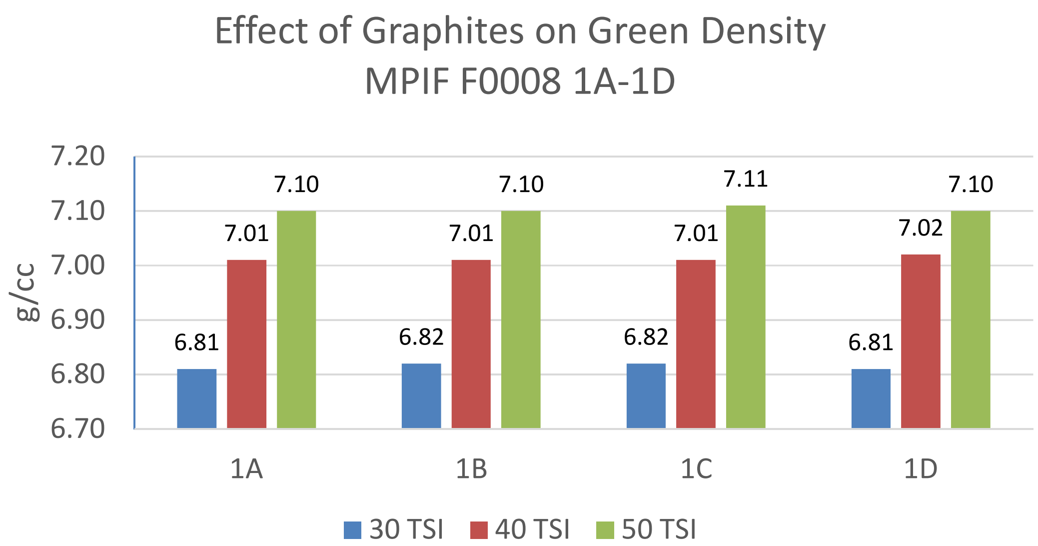
Powder Properties: Table 7 presents the Hall density and flow rate values for the twelve subject PM mixtures.

Mix Identity	Alloy	Hall Apparent Density, g/cc	Hall Flow Rate, sec./50g
1A	F0008	3.12	40
2A	FC0208	3.11	36
3A	FN0208	3.12	37
1B	F0008	3.10	36
2B	FC0208	3.10	38
3B	FN0208	3.10	36
1C	F0008	3.09	38
2C	FC0208	3.10	38
3C	FN0208	3.11	41
1D	F0008	3.07	39
2D	FC0208	3.09	38
3D	FN0208	3.11	40

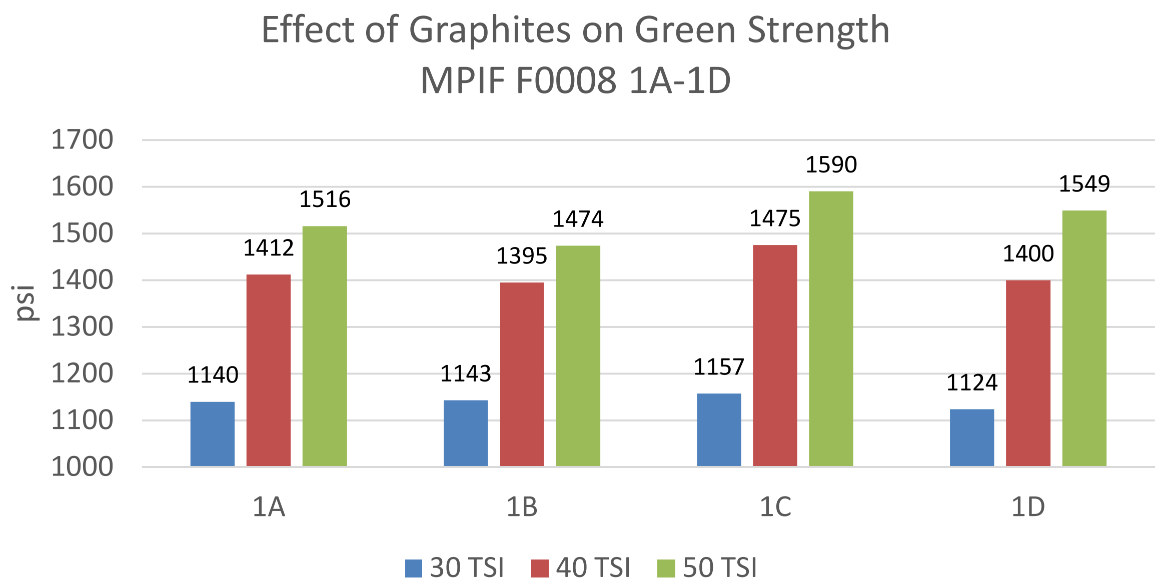
There is no significant difference in the Hall apparent density or flow rate of the mixtures that can be attributed to the graphite type. All of the Hall values fall within the typical ranges expected.

Green Properties: Green property measurements included Green Density, Green Strength, and % Green Spring from Die Size.

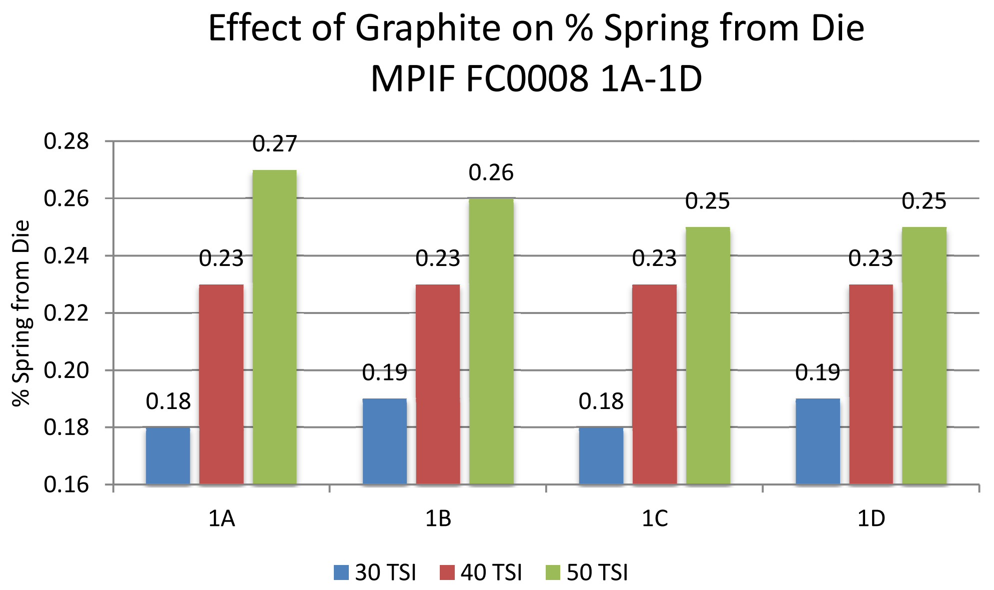
Effect of Graphite on Green Properties of MPIF F0008: Test results on Green Density and Green Strength are presented below in graphic format for each mixture combination.



No significant change in green density was observed between PM mixes containing flake graphite from different sources.

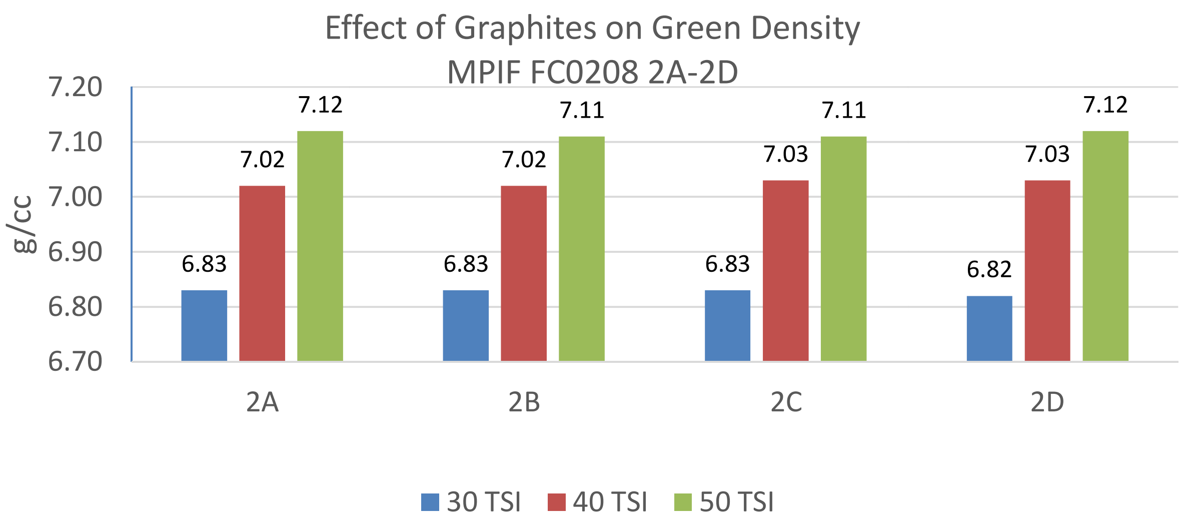


No significant differences in green strength were observed which can be attributed to graphite origin.

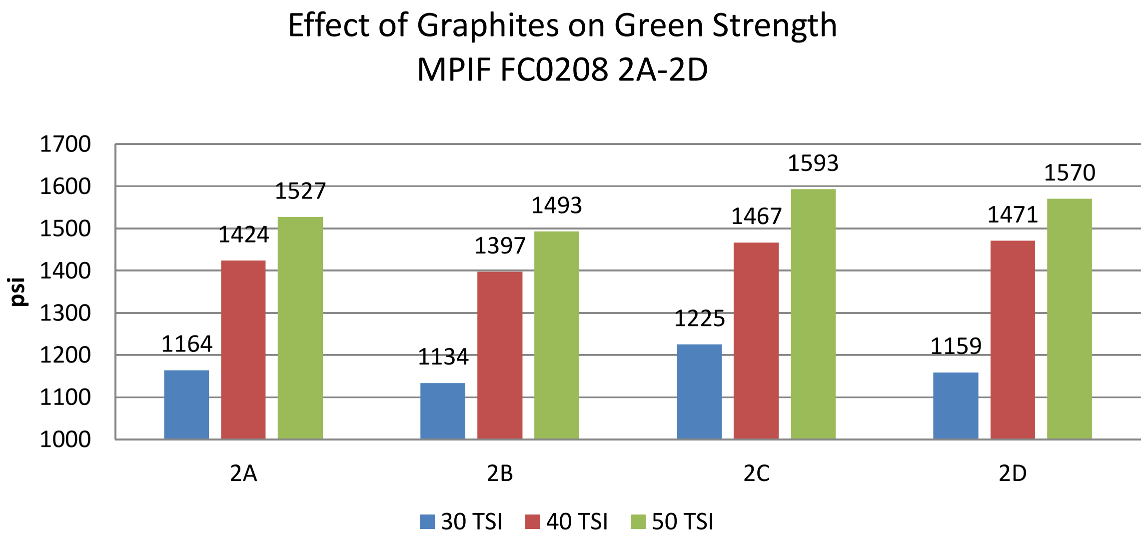


Differences in % Spring from Die between samples containing Chinese flake and Madagascar flake are unremarkable.

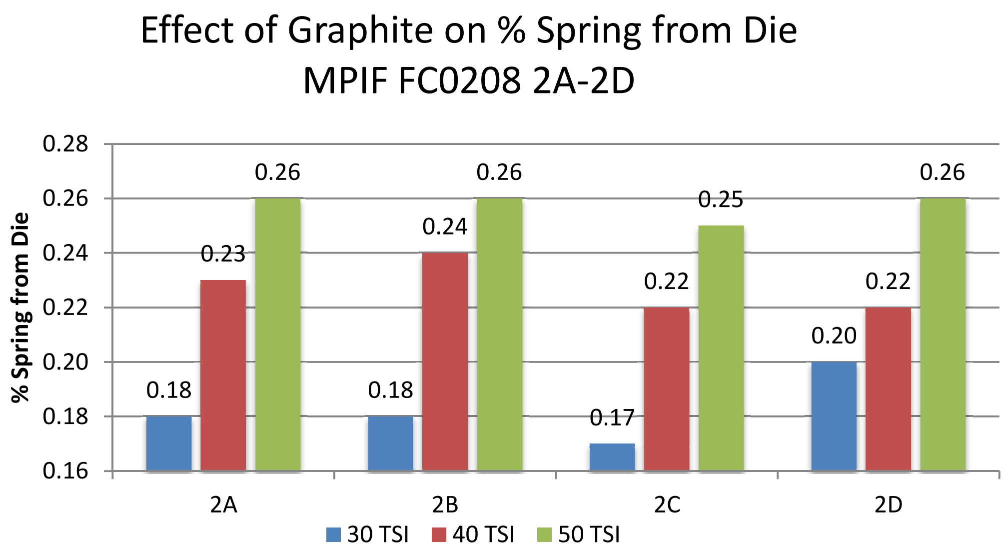
<u>Effect of Graphite on Green Properties of MPIF FC0208:</u>



Differences in Green Density between samples containing Chinese flake and Madagascar flake are unremarkable.

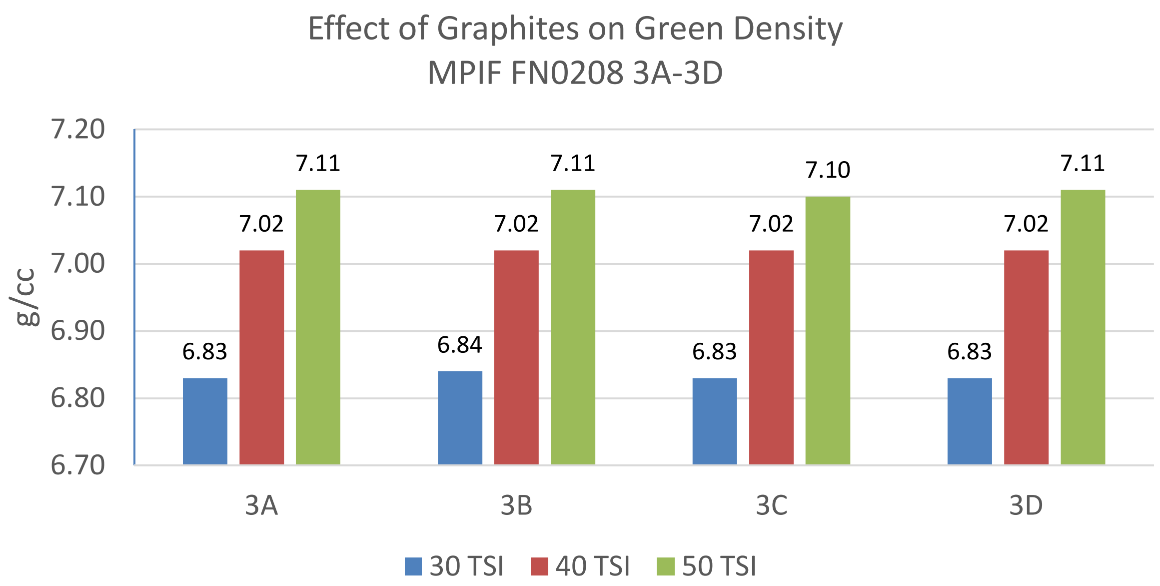


Differences in Green Strength between samples containing Chinese flake and Madagascar flake are unremarkable.

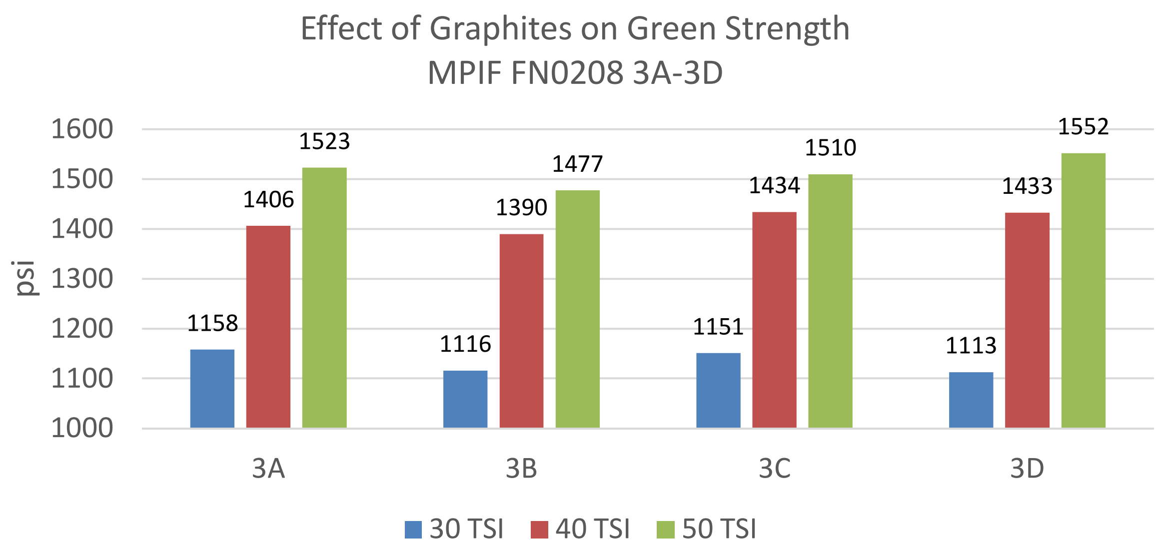


Differences in % Spring from Die are not considered significant.

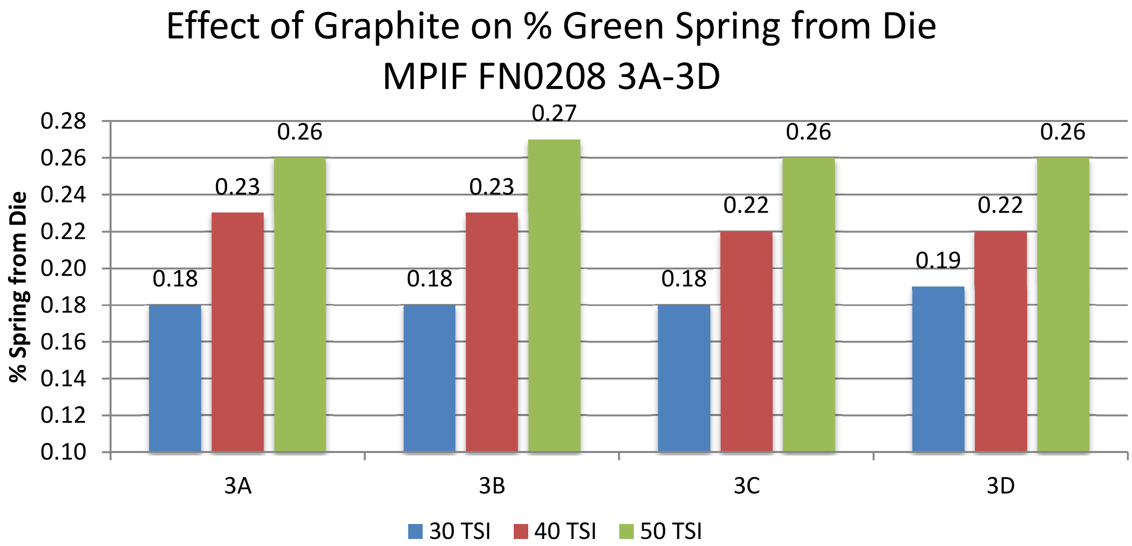
Effect of Graphite on Green Properties of MPIF FN0208:



Differences between samples containing Chinese flake and Madagascar flake are unremarkable.



Differences in Green Strength between samples containing Chinese flake and Madagascar flake are unremarkable.

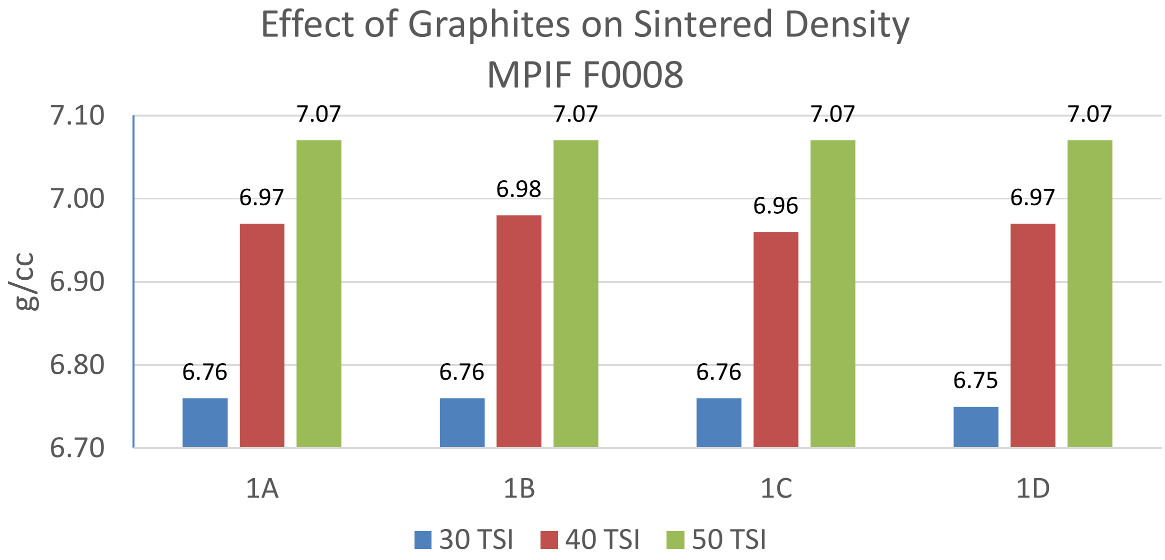


Differences in Spring from Die values between samples containing Chinese flake and Madagascar flake are not considered significant.

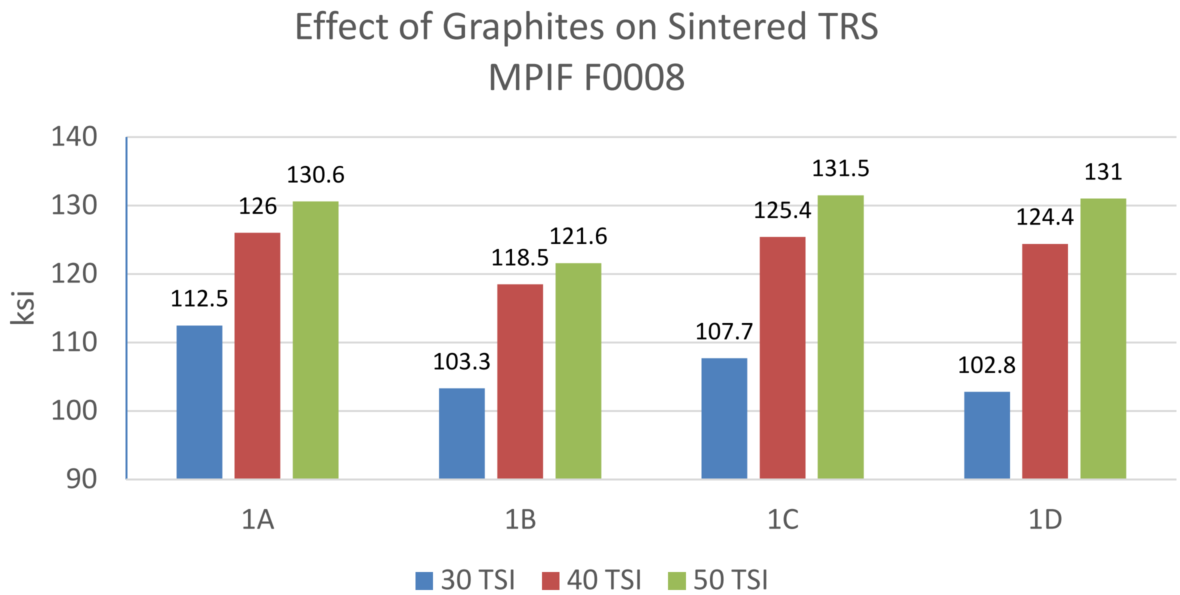
In summary, no significant differences in powder properties, green density, or green strength were observed between the three PM alloys containing 3203 or 1651 made with Chinese vs. Madagascar flake graphite.

Sintered Properties: Sintered properties were measured and include Sintered Density, Transverse Rupture Strength, Apparent Hardness, and % Dimensional Change from Die size

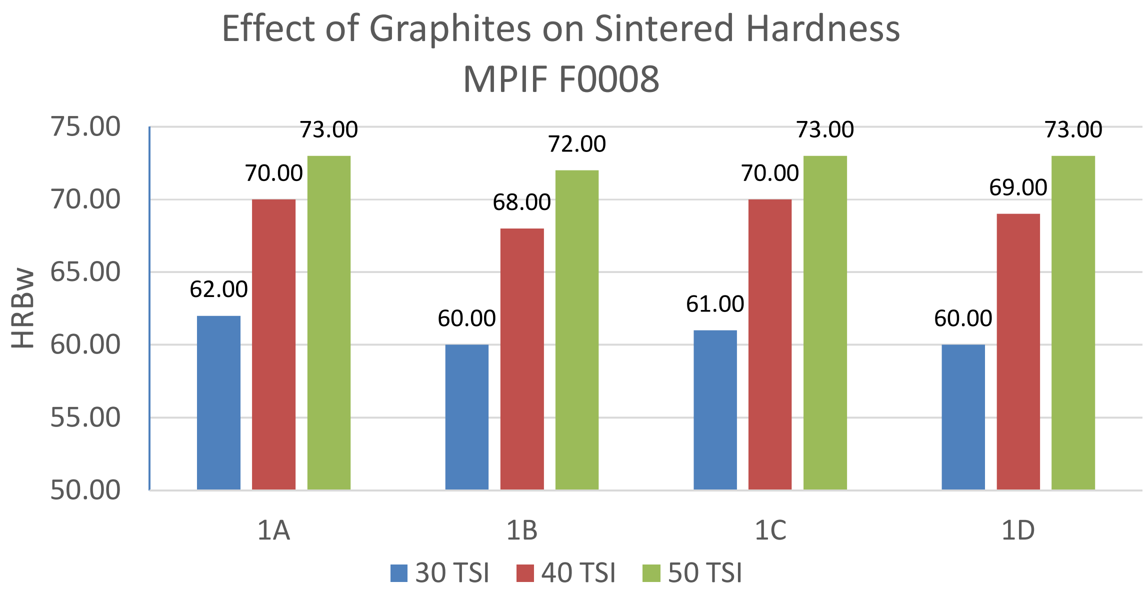
Effect of Graphite on Sintered Properties: MPIF F0008:: Test results of Sintered Density, Transverse Rupture Strength, Hardness, and Dimensional Change for F0008 alloy are presented in the following histogram plots.



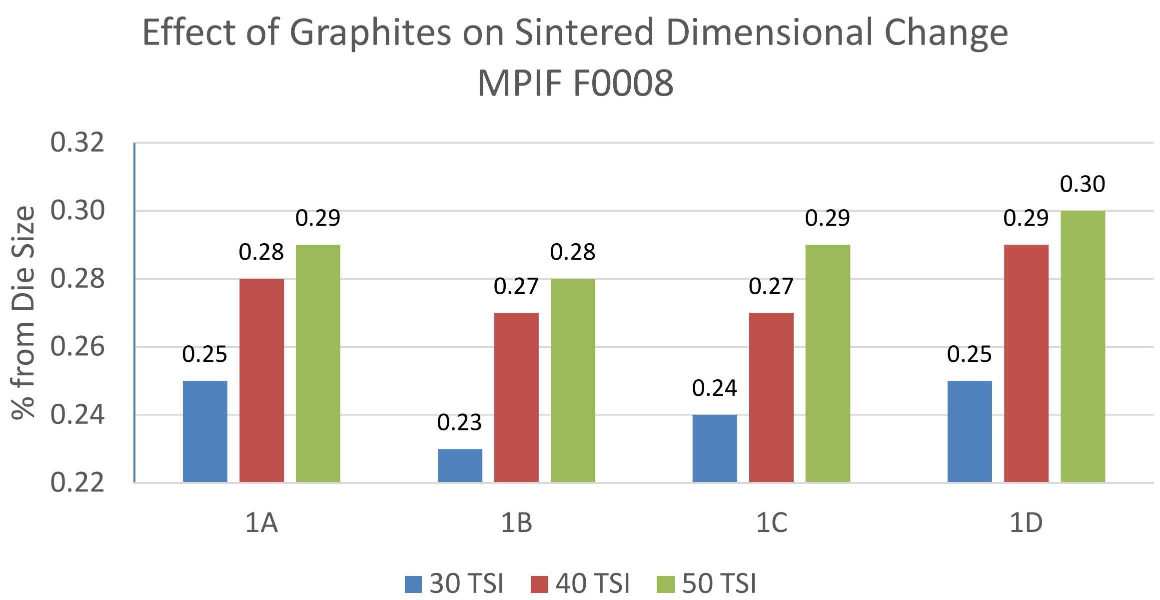
In the F0008 alloy evaluated, there is no significant difference in the sintered density of test bars pressed at 30 TSI, 40 TSI, or 50 TSI made with Chinese flake graphite vs. Madagascar flake graphite.



TRS bars pressed at 30 TSI, 40 TSI, and 50 TSI showed no significant different in rupture strength regardless of graphite origin.

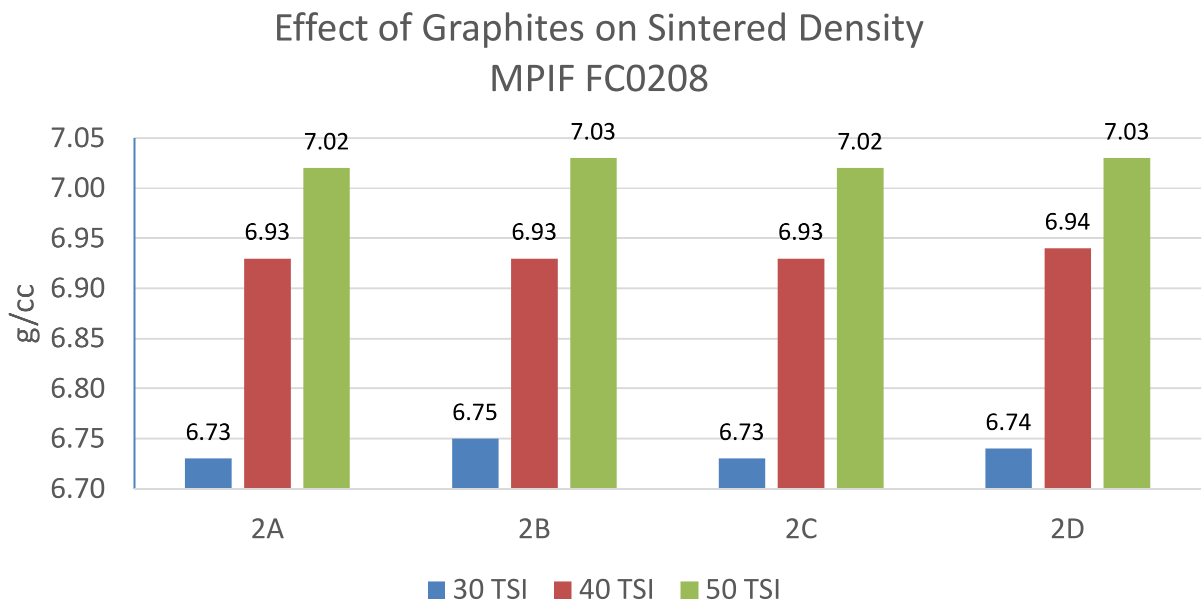


Asbury Carbons PM alloy graphite products 1651 and 3203 result in alloys with the same sintered hardness regardless of the geographical origin of the graphite feed stock.

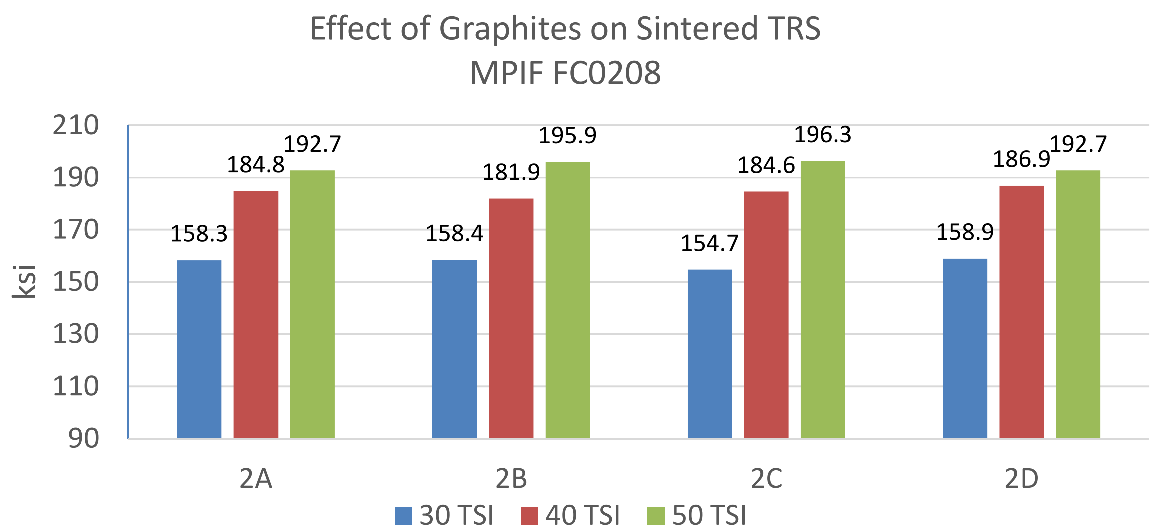


The differences in Sintered Dimensional Change between test specimens made with Asbury 1651 and 3206 alloy graphite powders are within the range expected.

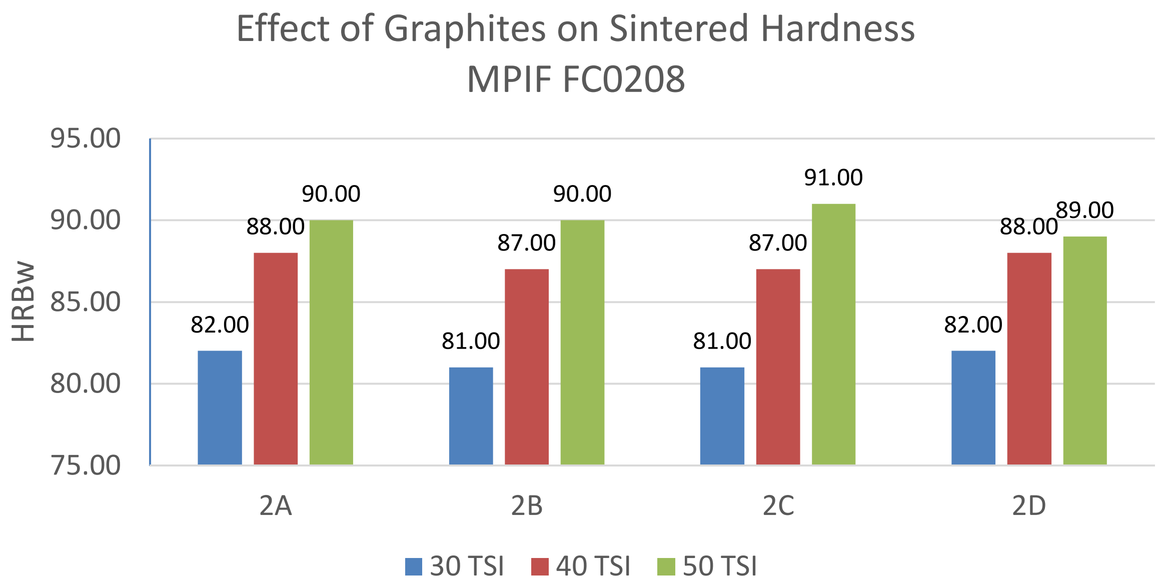
Effect of Graphite on Sintered Properties-MPIF FC0208 Alloy System: Test results of Sintered Density, Transverse Rupture Strength, Hardness, and Dimensional Change for an FC0208 alloy are presented in the following histograms.



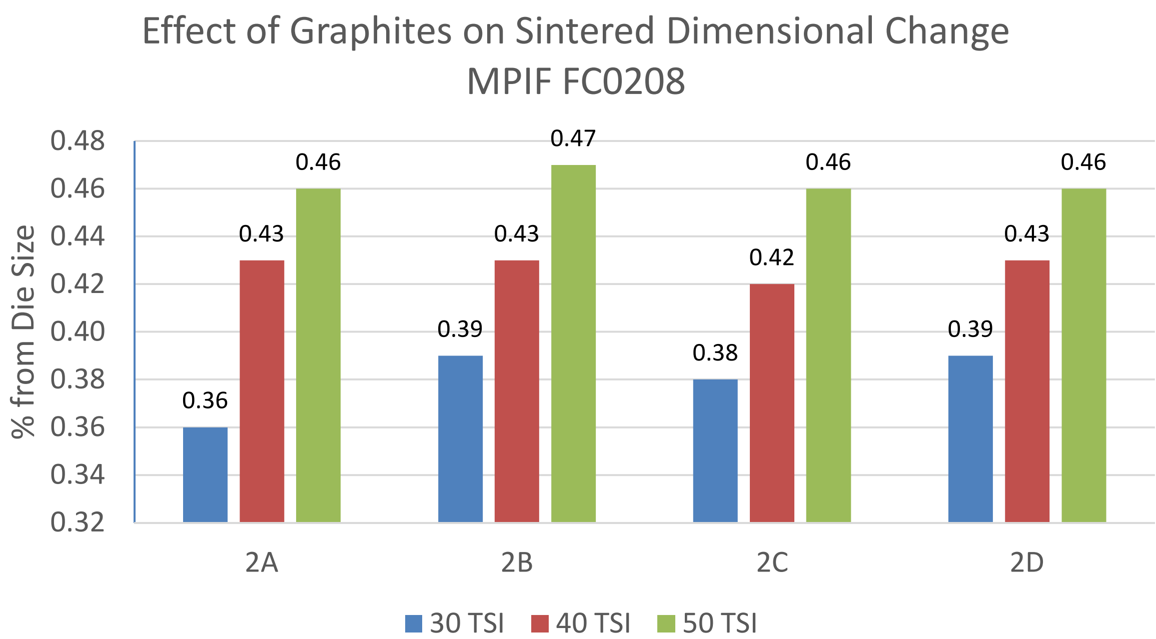
No significant differences in sintered density were observed in FC0208 test specimens made using Asbury 1651 and 3203 alloy graphite from different origins.



No significant differences in transverse rupture strength were observed in sintered FC0208 test specimens made using Asbury 1651 and 3203 alloy graphite from different origins.

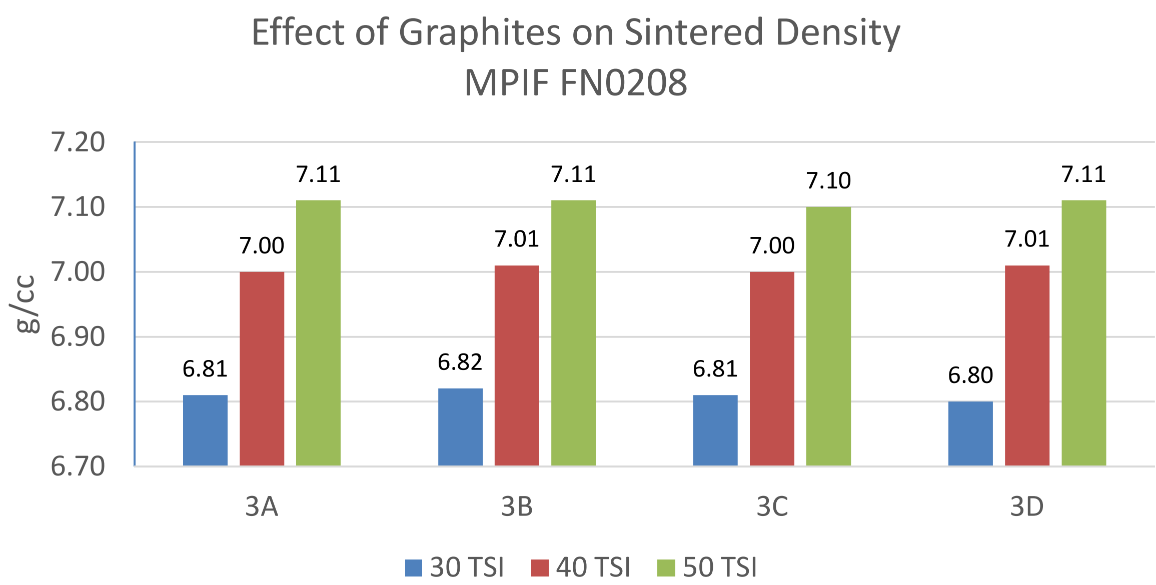


Sintered harness values for an FC0208 alloy using graphite powders from different geographical origins fall within expected ranges.

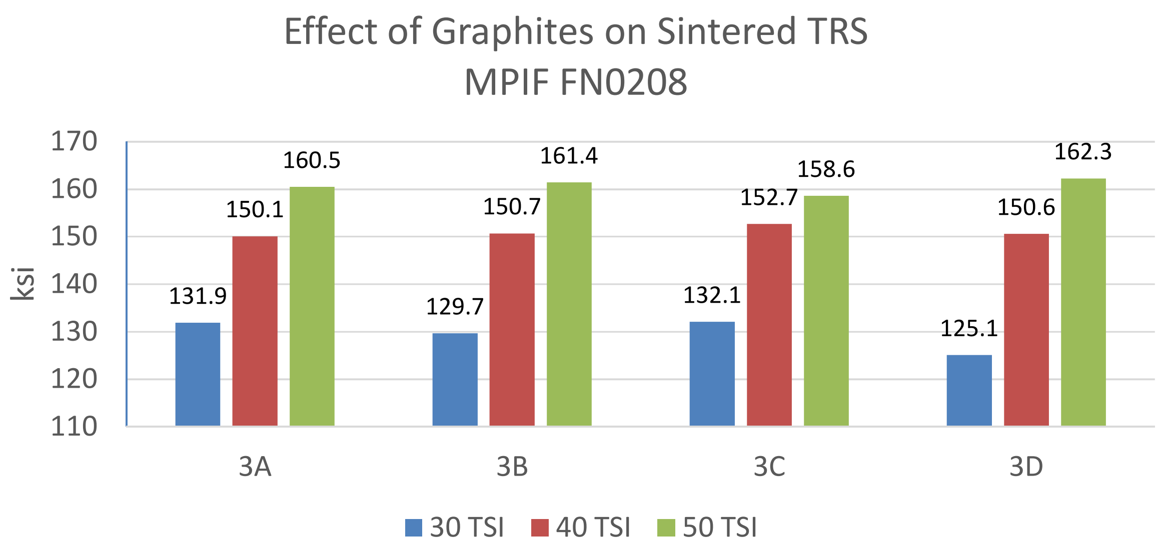


There is no significant difference between dimensional change values of an FC0208 alloy when using flake graphite from the different sources evaluated.

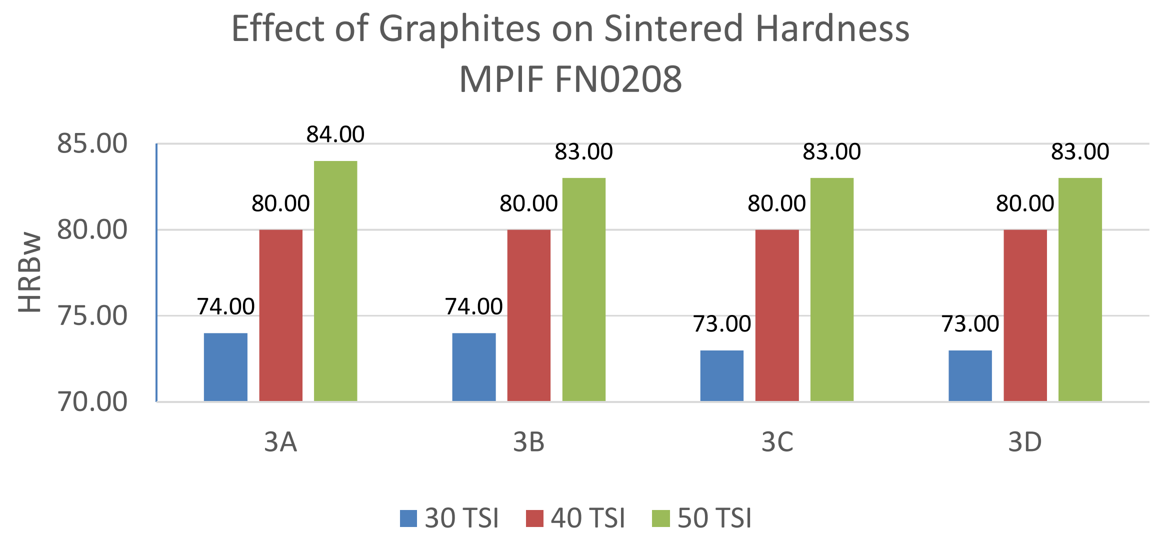
Effect of Graphite on Sintered Properties-MPIF FN0208 Alloy System: Test results of Sintered Density, Transverse Rupture Strength, Hardness, and Dimensional Change for an FN0208 alloy are presented in the following histogram plots.



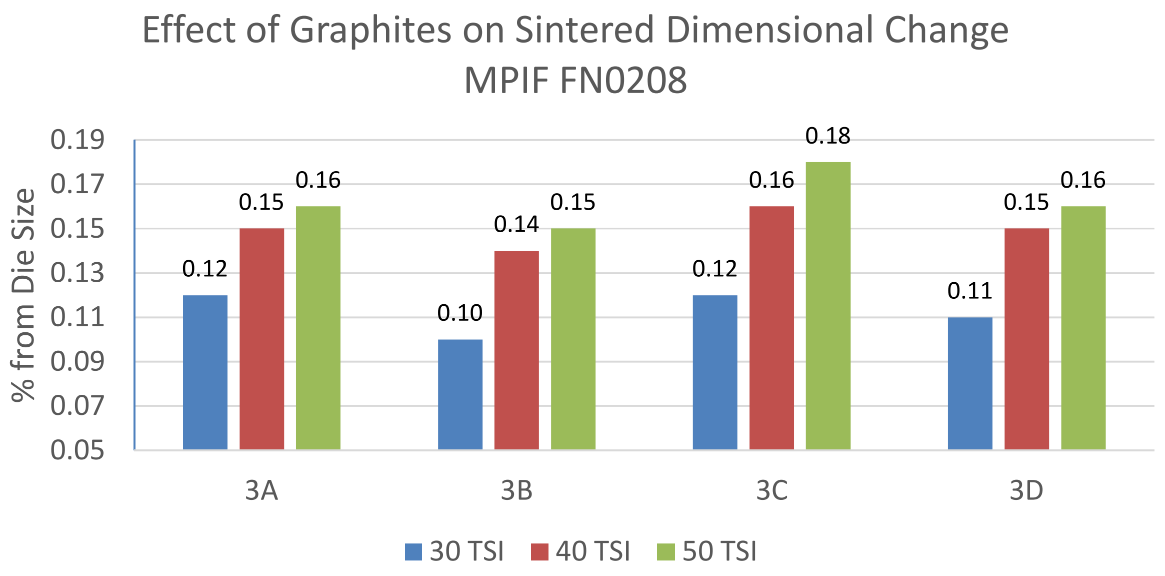
Sinter density values are typical and are virtually identical between test bars using graphite powder from the two sources studied.



There are no significant differences between TRS values of the FN0208 alloys based on the source graphite used in this study.



FN0208 alloys using the different sourced graphite materials studied have nearly identical sinter hardness values.



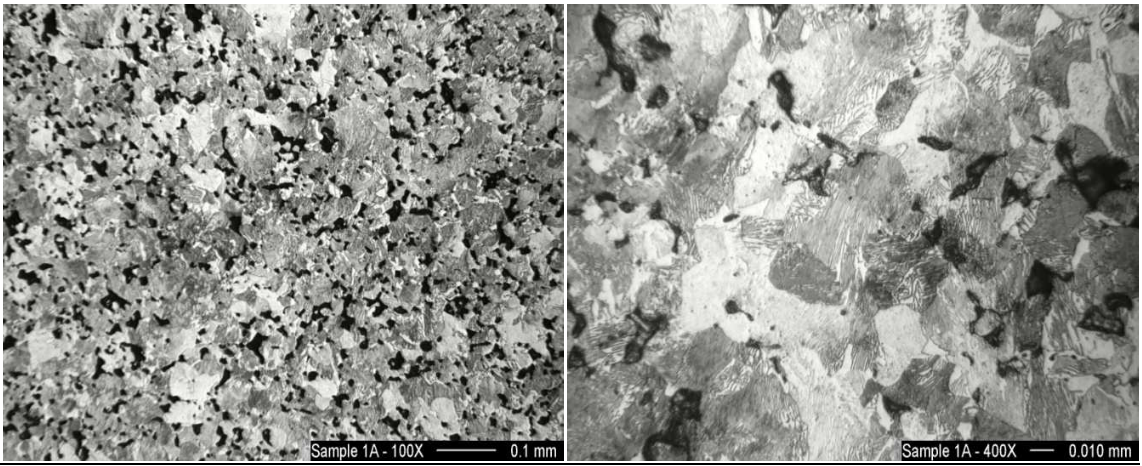
There is no significant difference in the sintered dimensional change between alloy bars containing 1651, or 3203 graphite powder manufactured from the different sources of graphite used in this study.

<u>Sintered-Bar Mechanical Testing Data Conclusions:</u> Test bars molded at 30, 40, and 50KSI were tested for Sintered Density, TRS, Sintered Hardness, and Dimensional Change. No significant differences in sintered properties were observed between PM formulations using graphite alloy powder milled to 3203 or 1651 specifications. No unique behavior or variation from expected test values occurred as a result of using powder manufactured from graphite originating from Madagascar. Test data was unremarkable and indistinguishable from that generated using conventional China sourced flake graphite.

Summary Results: A study to compare the performance of two powder metallurgy graphite alloy powders from different geographical locations was performed. Natural flake graphite originating from China and Madagascar were commutated and size-classified into two standard PM products: A nominal 5um powder (Asbury 3203), and a nominal 10um powder (Asbury 1651). Three PM alloys, FC0008, FC0208, and FN0208 were prepared using each graphite product. Test bars were prepared at 30, 40, and 50KSI compaction pressure. Testing was performed on the powders, green compacts, and sintered compacts. Metallographic specimens were prepared and examined. Based on the test results the PM alloy graphite powders made from Chinese-origin and Madagascar-origin flake graphite can be used interchangeably in FC0008, FC0208, and FN0208 alloy compositions.

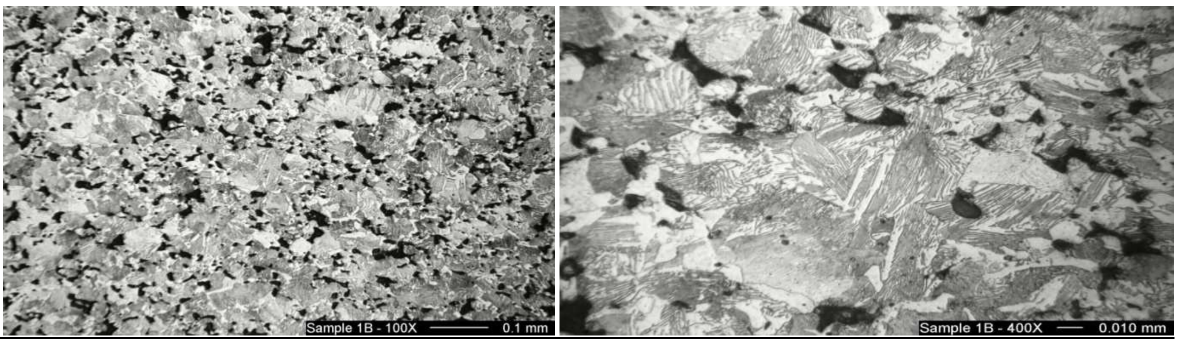
Appendix 1: Microstructure images and analysis: The following metallographic images, along with accompanying commentary, were provided by Product Assurance Services, Saint Marys PA.

Effect of Graphite on Sintered Microstructure – MPIF F-0008 Sample 1A



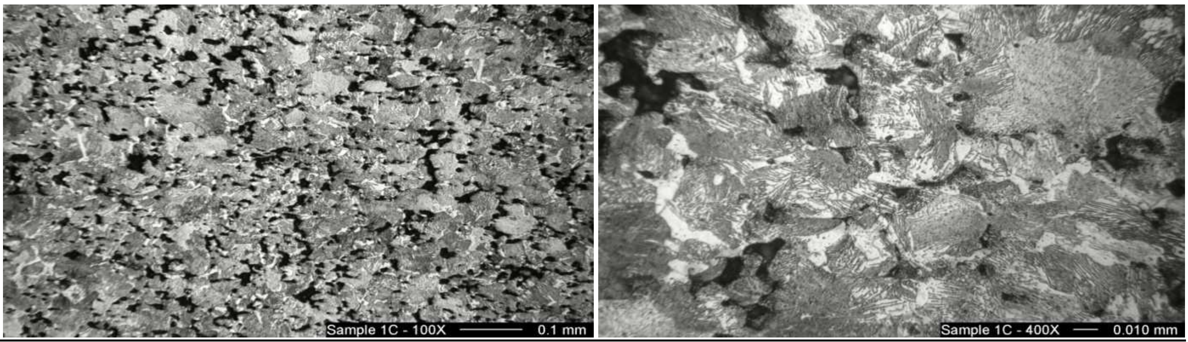
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF F-0008 Sample 1B



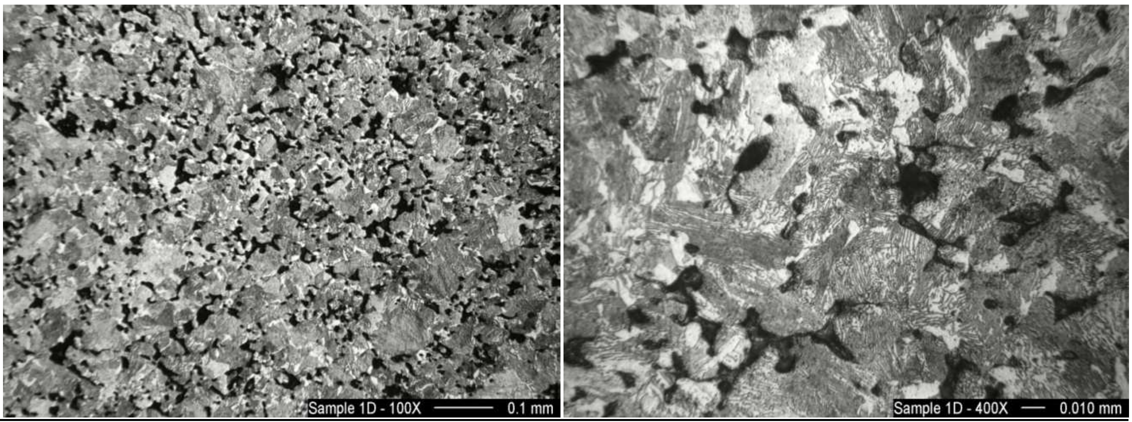
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF F-0008 Sample 1C



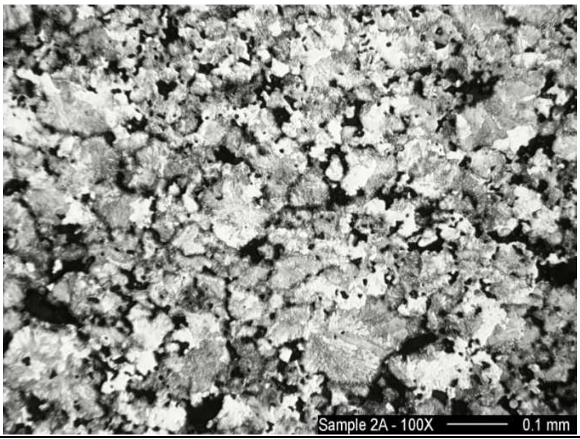
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. The degree of sinter was average, typical of a conventional sinter.

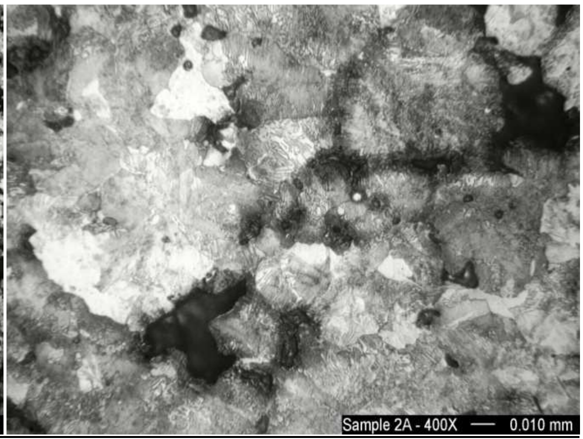
Effect of Graphite on Sintered Microstructure – MPIF F-0008 Sample 1D



The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. The degree of sinter was average, typical of a conventional sinter.

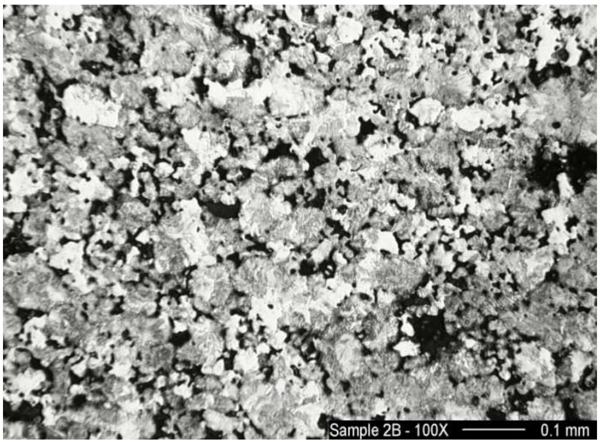
Effect of Graphite on Sintered Microstructure – MPIF FC-0208 Sample 2A

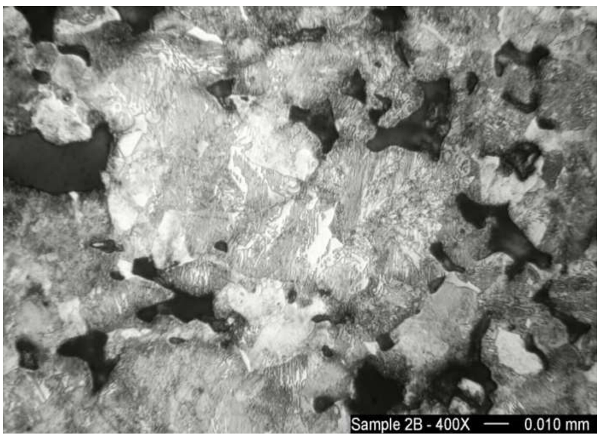




The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Isolated un-dissolved copper was seen throughout. The degree of sinter was average, typical of a conventional sinter.

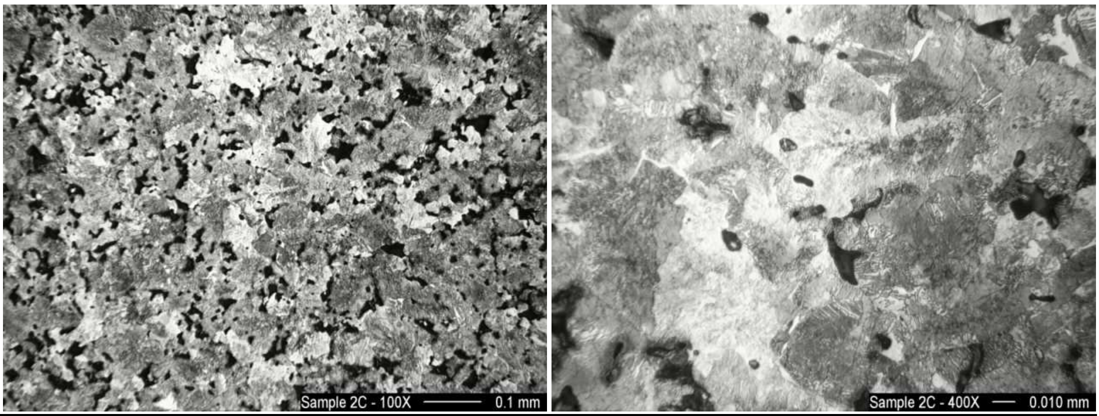
Effect of Graphite on Sintered Microstructure – MPIF FC-0208 Sample 2B





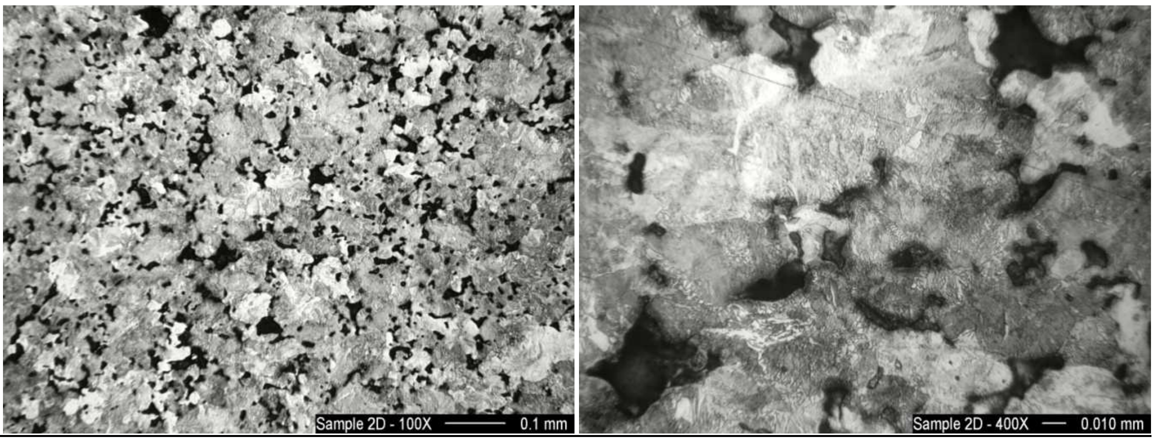
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Isolated un-dissolved copper was seen throughout. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF FC-0208 Sample 2C



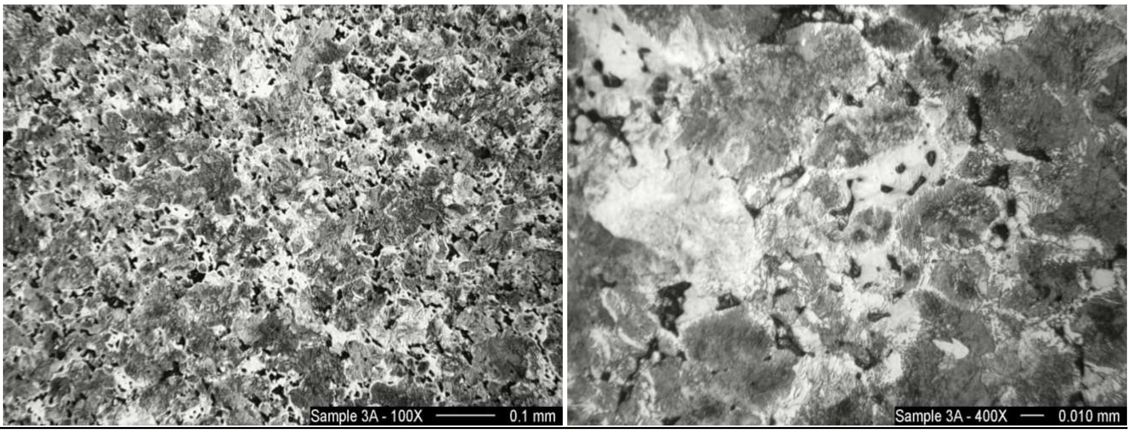
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Isolated un-dissolved copper was seen throughout. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF FC-0208 Sample 2D



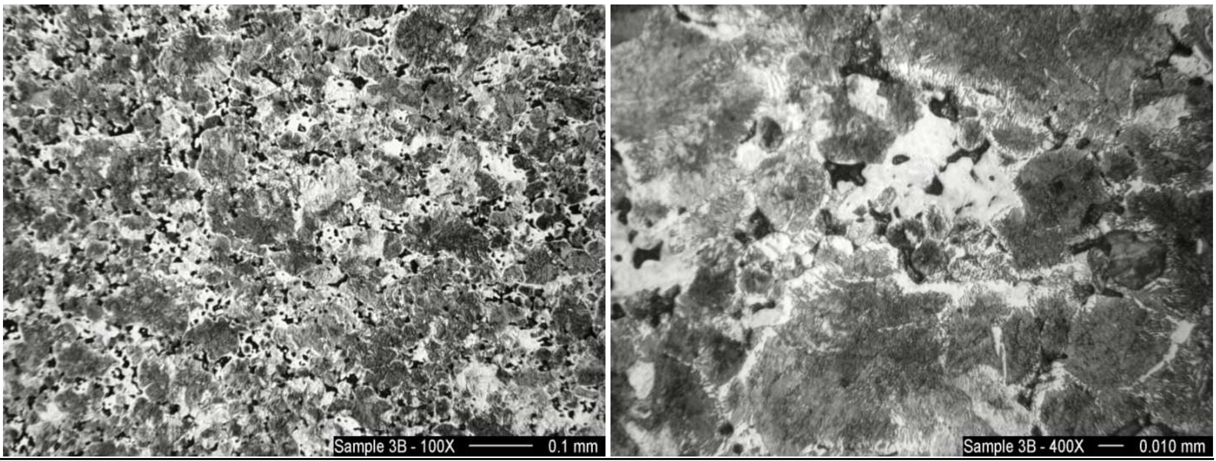
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Isolated un-dissolved copper was seen throughout. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF FN-0208 Sample 3A



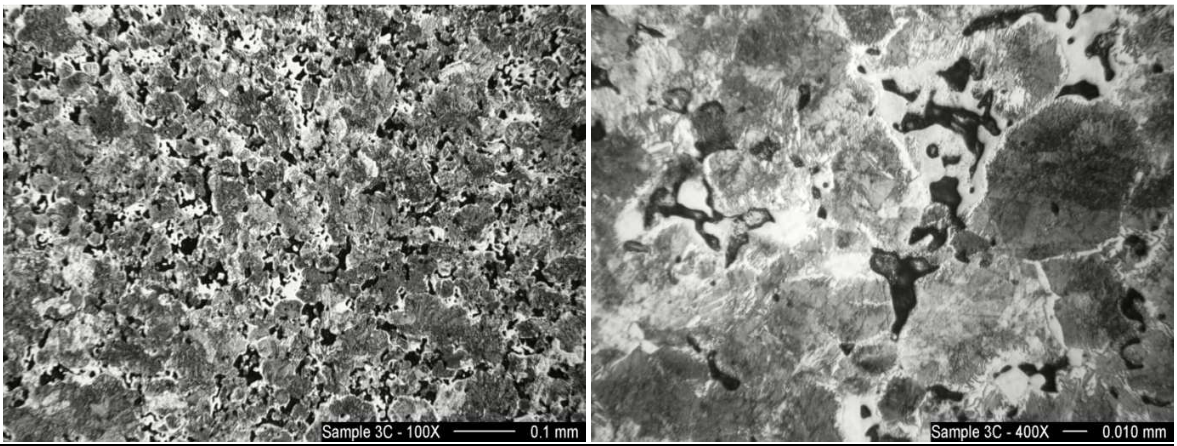
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Nickel-rich areas were seen throughout. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF FN-0208 Sample 3B



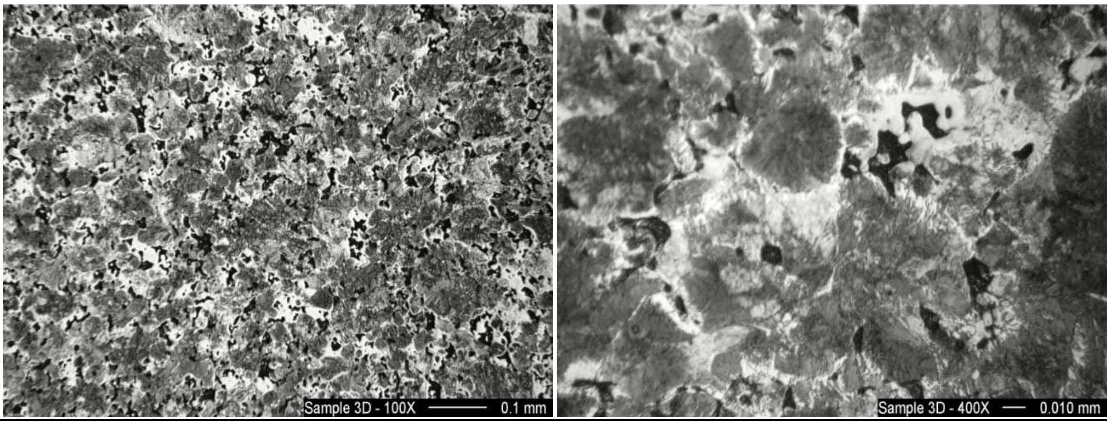
The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Nickel-rich areas were seen throughout. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF FN-0208 Sample 3C



The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Nickel-rich areas were seen throughout. The degree of sinter was average, typical of a conventional sinter.

Effect of Graphite on Sintered Microstructure – MPIF FN-0208 Sample 3D



The microstructure consisted of a uniform pearlitic structure with isolated ferrite. The estimated combined carbon level was 0.7-0.8% C. Nickel-rich areas were seen throughout. The degree of sinter was average, typical of a conventional sinter.

Conclusions based on observed microstructures: All microstructures were typical of those expected for MPIF Standard 35 compositions. No significant differences attributable to the different sources of graphite powder used were observed.

Appendix 2: Tabulated Green Part Test Data.

Green property value Table (each point represents an average of three test points):

Mix#	Compaction Pressure, TSI	Green Density, g/cc	Green Strength, psi	Green Spring From Die Size, %
1A	30	6.81	1140	0.18
	40	7.01	1412	0.23
	50	7.10	1516	0.27
1B	30	6.82	1143	0.19
	40	7.01	1395	0.23
	50	7.10	1474	0.26
1C	30	6.82	1157	0.18
	40	7.01	1475	0.23
	50	7.11	1590	0.25
1D	30	6.81	1124	0.19
	40	7.02	1400	0.23
	50	7.10	1549	0.25
2A	30	6.83	1164	0.18
	40	7.02	1424	0.23
	50	7.12	1527	0.26
2B	30	6.83	1134	0.18
	40	7.02	1397	0.24
	50	7.11	1493	0.26
2C	30	6.83	1225	0.17
	40	7.03	1467	0.22
	50	7.11	1593	0.25
2D	30	6.82	1159	0.20
	40	7.03	1471	0.22
	50	7.12	1570	0.26
3A	30	6.83	1158	0.18
	40	7.02	1406	0.23
	50	7.11	1523	0.26
3B	30	6.84	1116	0.18
	40	7.02	1390	0.23
	50	7.11	1477	0.27
3C	30	6.83	1151	0.18
	40	7.02	1434	0.22
	50	7.10	1510	0.26
3D	30	6.83	1113	0.19
	40	7.02	1433	0.22
	50	7.11	1552	0.26

Appendix 3: Sintered Test Data:

Sinter property values (each point represents an average of three test points):

Mix#	Compaction Pressure, TSI	Sintered Density, g/cc	TRS, ksi	Apparent Hardness, HRBw	DC from Die Size, %
1A	30	6.76	112.5	62	0.25
	40	6.97	126.0	70	0.28
	50	7.07	130.6	73	0.29
1B	30	6.76	103.3	60	0.23
	40	6.98	118.5	68	0.27
	50	7.07	121.6	72	0.28
1C	30	6.76	107.7	61	0.24
	40	6.96	125.4	70	0.27
	50	7.07	131.5	73	0.29
1D	30	6.75	102.8	60	0.25
	40	6.97	124.4	69	0.29
	50	7.07	131.0	73	0.30
2A	**30**	**6.73**	**158.3**	**82**	**0.36**
	40	6.93	184.8	88	0.43
	50	7.02	192.7	90	0.46
2B	30	6.75	158.4	81	0.39
	40	6.93	181.9	87	0.43
	50	7.03	195.9	90	0.47
2C	30	6.73	154.7	81	0.38
	40	6.93	184.6	87	0.42
	50	7.02	196.3	91	0.46
2D	30	6.74	158.9	82	0.39
	40	6.94	186.9	88	0.43
	50	7.03	192.7	89	0.46
3A	**30**	**6.81**	**131.9**	**74**	**0.12**
	40	7.00	150.1	80	0.15
	50	7.11	160.5	84	0.16
3B	30	6.82	129.7	74	0.10
	40	7.01	150.7	80	0.14
	50	7.11	161.4	83	0.15
3C	30	6.81	132.1	73	0.12
	40	7.00	152.7	80	0.16
	50	7.10	158.6	83	0.18
3D	30	6.80	125.1	73	0.11
	40	7.01	150.6	80	0.15
	50	7.11	162.3	83	0.16