SPECIALTY CARBONS FOR **POWDER METALLURGY**

ENSACO®
Carbon Black

TIMREX®
Graphite

IMERYS

POWDER METALLURGY – HOW TO SHAPE PERFORMING SOLUTIONS

INNOVATIVE LEADERSHIP

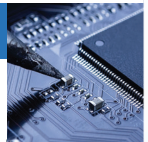
Innovative leadership and capabilities make Imerys Graphite & Carbon the right partner for the development and optimization of solutions for powder metallurgy.

Imerys Graphite & Carbon has been serving this market for more than two decades, always aligning to new developments and opportunities in the different applications.

Close collaboration with customers led to graphite based solutions that ensure consistent reliable and high performance metal powders.

The range of products also includes different grades of carbon black solutions ideal for mixing with the latest high performing alloys.

Efficient sintering, high purity, high crystallinity, flowability and the right particle-size distribution are some of the main characteristics that Imerys Graphite & Carbon offers to the market for high quality performance powder metallurgy.



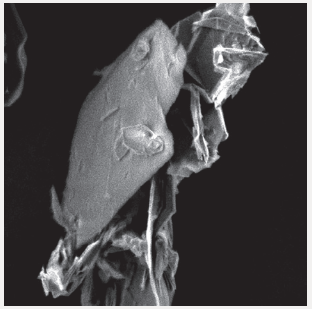
IMERYS GRAPHITE & CARBON SOLUTIONS FOR POWDER METALLURGY

CUSTOMIZABLE SOLUTIONS

Imerys Graphite & Carbon delivers tailor made solutions for Powder Metallurgy applications with superior consistency of key product parameters:
Purity, crystallinity, particle size distribution, and oversize control.

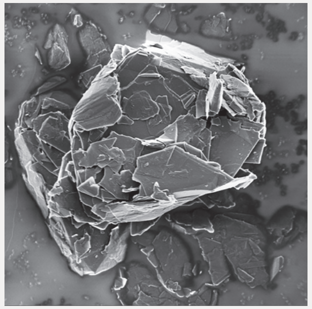
KEY REQUIREMENTS OF PM PARTS MANUFACTURING	BENEFIT FROM IMERYS	RECOMMENDED GRADE
High mechanical performance High dimensional stability Sinter-hardening Complex shape	Defined raw material and process for synthetic graphite High consistency and tight specifications of key properties (ash, moisture, particle size, crystallinity)	Primary synthetic graphites: TIMREX® F 10 TIMREX® F 25 TIMREX® KS 44
Reduction of PM parts cost (lower raw-material cost)	Full control of supply chain for natural graphite	Natural graphites: TIMREX® PG 10 TIMREX® PG 25 TIMREX® PG 44
Oxides reduction Improved flowability of powder mix	Defined raw material and process for carbon black High consistency and tight specifications of key properties (ash, moisture)	Carbon black: ENSACO® 250G

GRAPHITE & CARBON POWDERS



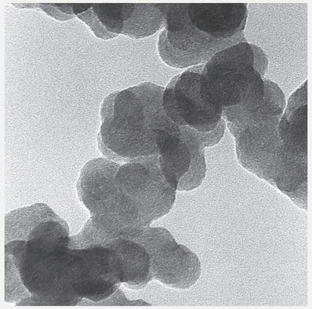
NATURAL GRAPHITE

- High crystallinity and anisotropy
- Consistent purity (96-97%)



PRIMARY SYNTHETIC GRAPHITE

- High purity (> 99%)
- Smaller, isotropically oriented crystallites
- Suited for high-performance end applications



CARBON BLACK

- High purity (> 99%)
- High specific surface area
- High structure

KEY BENEFITS – PRIMARY SYNTHETIC GRAPHITE VERSUS NATURAL GRAPHITE

FLOWABILITY

Primary synthetic or natural, with d90 in the range of 10 µm - 44 µm, has no significant impact on PM mixes' flowability [1].

GRAPHITE TYPE	APRROX. d90 (µm)	A: HALL FLOW RATE (s/50 g)	B: HALL FLOW RATE (s/50 g)
Natural 10	10	32	34
Natural 25	25	–	36
TIMREX® F10	10	33	35
TIMREX® PG10	10	33	35
TIMREX® PG25	25	34	36
TIMREX® F25	25	33	34
TIMREX® KS44	44	33	–
TIMREX® PG44	44	33	–

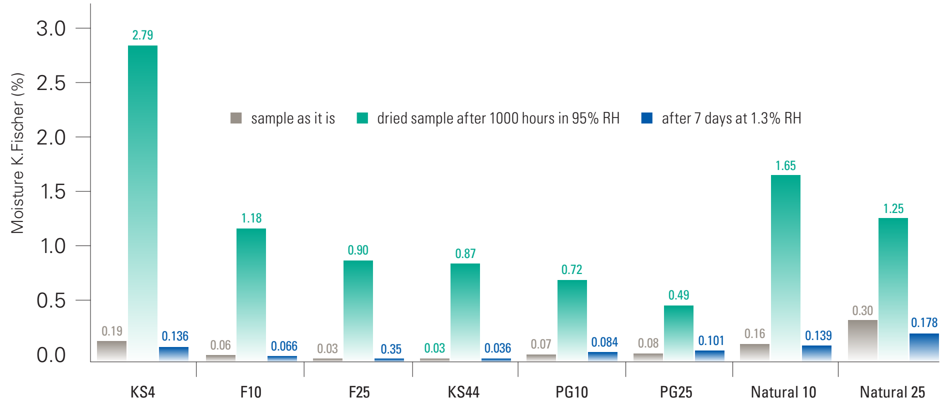
Hall Flow Rate of several powder mixes containing synthetic and natural graphites of three different particle size distributions: 10µm, 25µm, 44µm are d90 values. A: ANCORSTEEL B +0.65%C +2%Cu +0.8% wax. [Courtesy of Hoeganaes Corporation Europe]. B: ATOMET DB46 +0.6%C + 0.6% wax [courtesy of QMP - Rio Tinto Powders]

Consistent, fast flowability is connected to PM parts weight stability. Slight gain in weight standard deviation (8 to 9%) when shifting from 10 µm to 25 µm d90 natural graphite has been reported [1, Application Case 1]. In order to prevent the risk of fine powders dusting, it is typically recommended to limit the use of graphite powders with d90 lower than 10 µm to bonded mixes only [2, 3].

LOW MOISTURE ABSORPTION

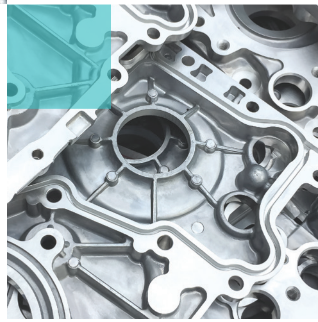
Imerys graphites have a lower moisture absorption compared to competitor grades at similar particle size distribution.

- Moisture uptake increases with decreasing particle size
- After drying, moisture returns to initial values
- TIMREX® PG25 has the lowest moisture absorption



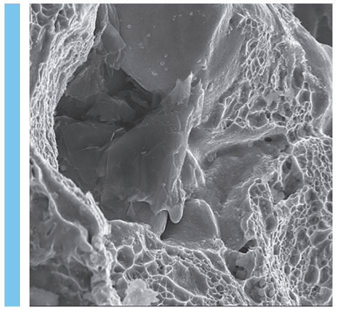
Water content – The method is based on the chemical reaction of water with sulphur dioxide and iodine (Karl Fischer Titration).

KEY BENEFITS – PRIMARY SYNTHETIC GRAPHITE

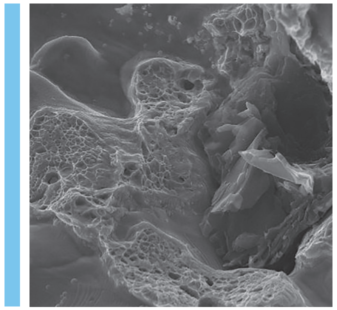


IMPROVED SINTERING PROCESS

- Enhanced iron oxides reduction activity for primary synthetic graphite compared to natural graphite, therefore carbon diffusion starts at lower temperatures
- Prolonged effective sintering time for better sinter necks formation or shorter sintering time
- Higher alloyed carbon in sintered PM parts, lower dimensional change sintered-to-die, slightly higher mechanical performance



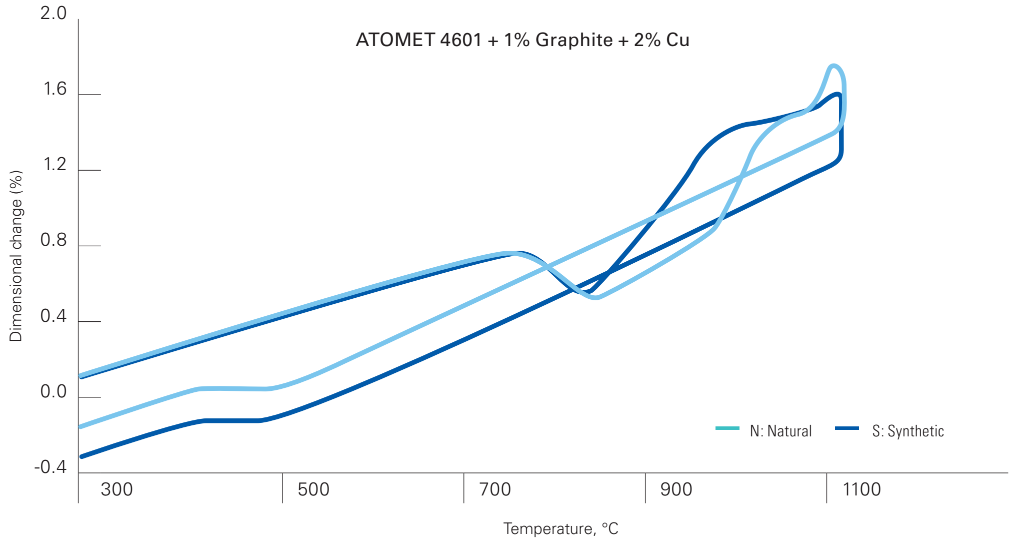
Fracture surface of PM compacts utilizing natural graphite PG10 (to the left) and primary synthetic graphite F10 (to the right) in a Höganäs AB AstaloyCrM+0.5%C mix. Heating performed in dilatometer in 90%N2/10%H2 atmosphere to 1120°C.



The earlier formation of sintering necks allowed by primary synthetic graphite F10, compared to natural flakes of the same particles size distribution is confirmed by finer dimples fracture in sinter-necks fracture surfaces [Chalmers University, Sweden].

IMPROVED DIMENSIONAL STABILITY

- High reproducibility of sintered dimensions resulting in enhanced quality of PM parts production
- Cost reduction due to less sizing, machining, and parts that are out of specification in lot-to-lot inspections



S. St-Laurent, E. Ilia, "Improvement of Dimensional Stability of Sinter Hardening Powders under Production Conditions", World PM 2010 Conference, Florence, Italy (2010).

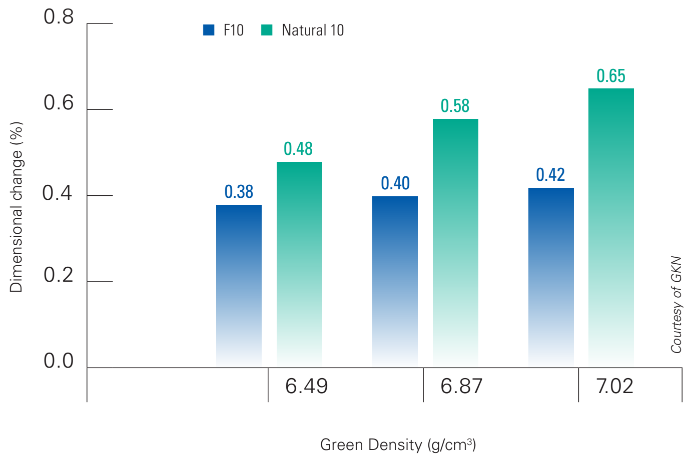
KEY BENEFITS – PRIMARY SYNTHETIC GRAPHITE

DIMENSIONAL CHANGE

Primary synthetic graphite shows lower, more stable dimensional charge at different densities.

SC 100.26 + 0.5% C + 0.75% Kenolub P11 + 0.5% MnS + 3% Cu

Sintering conditions: 1120°C for 25 minutes in Endogas



The high reproducibility of sintered dimensions results in enhanced quality of PM parts production. Possible cost reductions due to less sizing, machining, parts out of specification in lot-to-lot inspections are also to be considered.

Primary synthetic graphite shows lower, more stable dimensional change.

ASC 11.29 + 0.8% C + 0.8% Zn Stearate(STARMIX)

Sintering Conditions: 1120°C for 30 minutes in N2/H2 Number of Parts – 2000

GRAPHITE GRADE	SINTERED DENSITY (g/cm^3)	DIMENSIONAL CHANGE STD. DEV. (%)
F10	7.11	**0.008**
Natural 10	7.13	0.018

Courtesy of Höganäs AB

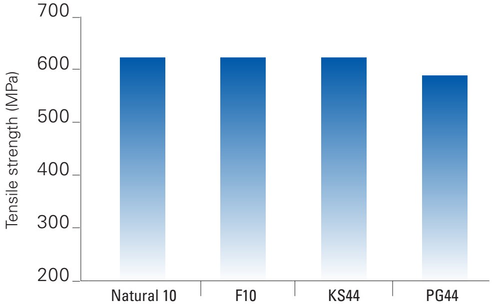
KEY BENEFITS – PRIMARY SYNTHETIC GRAPHITE

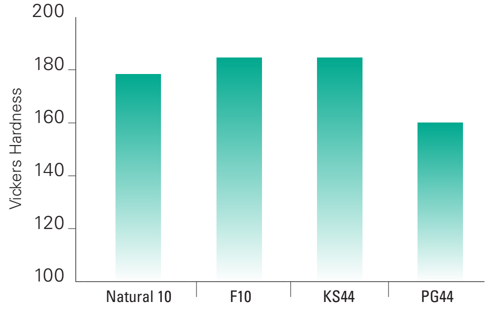
IMPROVED MECHANICAL PERFORMANCE

Synthetic graphite diffuses completely before Cu diffusion, resulting in higher Sintered Density HV, TS when compared to natural graphite.

Fe + 0.6% Lubricant + 2% Cu + 0.8% C

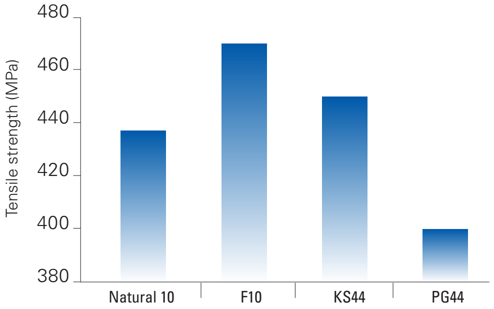
Sintering conditions: 1120°C for 30 minutes in N2/H2

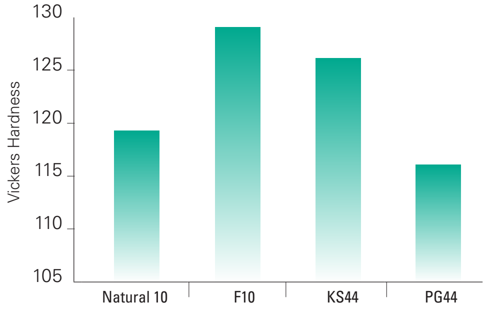




Fe + 0.6% Lubricant + 0.8% C

Sintering conditions: 1120°C for 30 minutes in N2/H2





Courtesy of Höganäs and KTH University

KEY BENEFITS – SYNERGIES BETWEEN SYNTHETIC GRAPHITE & CARBON BLACK

OXIDES REDUCTION

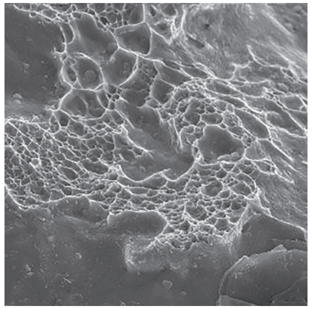
TIMREX® primary synthetic graphites and ENSACO® 250G carbon black have been shown to boost oxide reduction in a narrow temperature range during the pre-sintering stage.

- Astaloy CrM +0.6% Kenolube +0.5%C
- Charpy Test bars (10x10x55mm – ISO5754)
- Compaction at 600MPa
- Sintering in 90/10 N2/H2 atmosphere

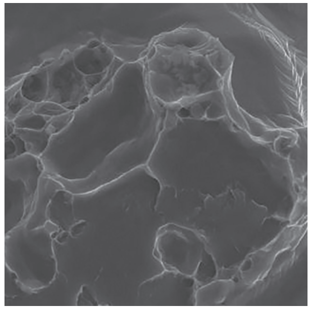
	~ d90 (µm)	TG-ONSET TEMP. (°C)	1ST DTG PEAK (°C) SURFACE OXIDE LAYER	2ND DTG PEAK (°C) STABLE SURFACE OXIDES AND COMPLEX INTERNAL OXIDES
TIMREX® PG10	10	1009.3	1079.2	1200.4
TIMREX® PG25	25	1034.6	1107.0	1199.2
TIMREX® F10	10	1011.7	1087.1	1192.0
TIMREX® F25	25	1029.6	1106.1	1200.5
TIMREX® KS4	4	996.4	1079.4	1200.1
ENSACO® 250G	–	**1007.6**	**1066.0**	**1189.9**

- Carbon black shows low TG-onset (early carbon diffusion)
- Oxide reduction starts at lower temperatures with ENSACO® 250G

- Unreacted graphite is visible on fracture surfaces for the coarser grades, especially TIMREX® PG25
- Reduction of surface oxides and even thermodynamically stable oxides is improved with finer graphite, by shifting from natural to synthetic graphite and by the use of ENSACO® Carbon black
- No carbon black residue is observed on the fracture surface, indicating its full dissolution
- Large fraction of cleavage facets indicates strong developed inter-particle necks



TIMREX® PG25



ENSACO® 250G

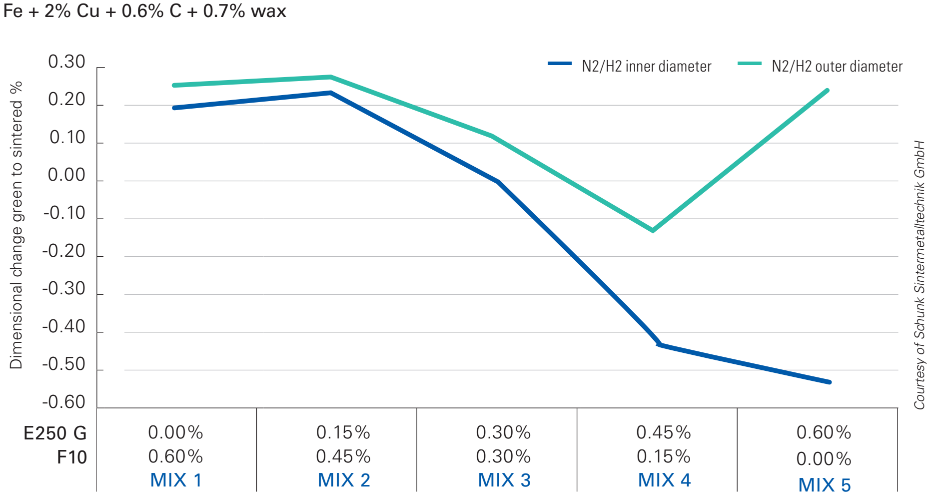
Courtesy of Chalmers University

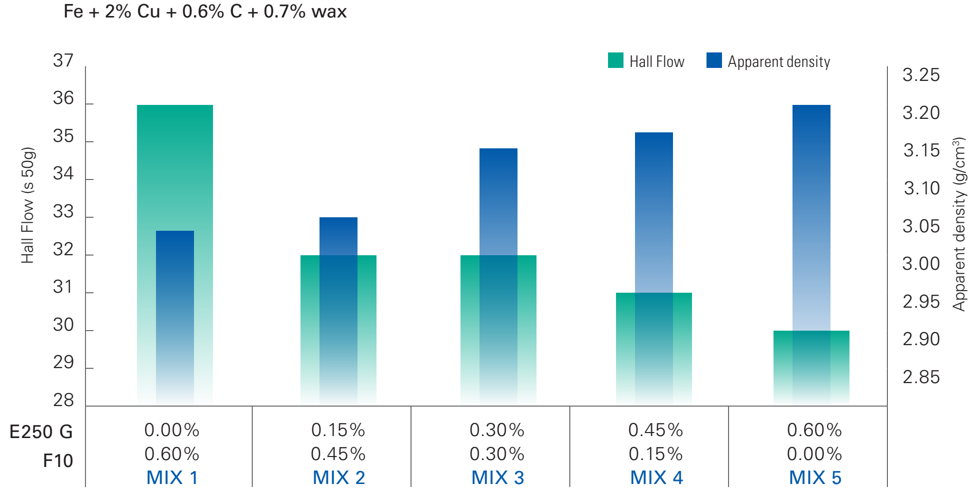
SYNERGIES BETWEEN GRAPHITE & CARBON BLACK

SYNERGIES BETWEEN GRAPHITE & CARBON BLACK

Partial substitution of primary synthetic graphite (F10) with conductive carbon black **ENSACO® 250G** can synergistically improve overall properties of Fe-Cu-C systems such as:

- Flowability and apparent density of powder mix
- Reduced weight scatter of green parts
- Dimensional stability after sintering



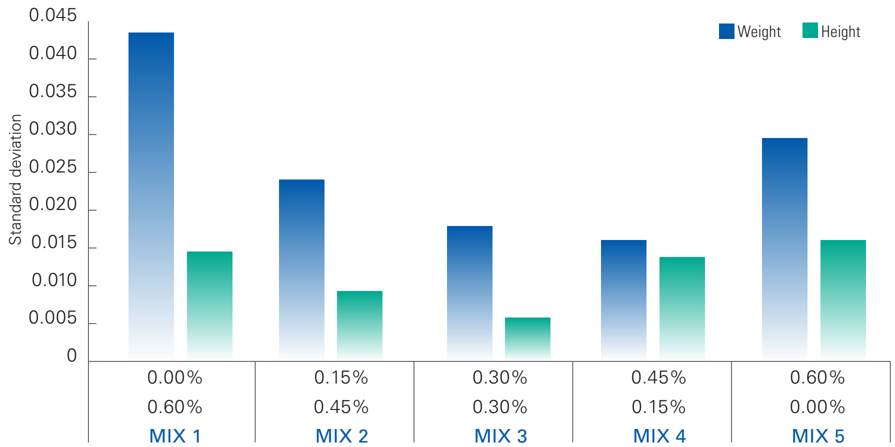


Increased springback is the drawback of using carbon black in PM Mixes. Addition of more than 0.3% carbon black leads to cracks in green part.

SYNERGIES BETWEEN GRAPHITE & CARBON BLACK / APPLICATION CASES

SYNERGIES BETWEEN GRAPHITE & CARBON BLACK

Scatter of Weight and Height 50 pcs.



Partial substitution of graphite F10 with carbon black ENSACO® 250 G can reduce height and weight scatter of the green parts.

These findings point in the direction of benefits achieved by minor additions of carbon black, as a sintering-booster. The PM Industry could consider a carbon package (graphite + carbon black), depending on the sintering atmosphere and PM parts geometry, size.

We recommend considering finer, synthetic graphite and carbon black additions to the mix in case of larger, higher density parts, where oxides reduction and therefore sintering quality mostly rely on the "carbon package" rather than on the reducing sintering atmosphere.

APPLICATION CASES

PURPOSE OF CARBON	PM MATERIALS	APPLICATIONS
Hardening by oxides reduction and solid state diffusion	Fe-based PM grades	**Structural engineering components:** - Chromium- based steel - Valve guides/seats
Solid state lubrication and friction moderation	Cu/Bronze-PM grades	**Self-lubricating engineering parts:** - Bearings, - Bushes, - Valve guides, - Valve seats
	Fe-based PM grades	**Friction materials:** - Sintered brake pads, - Clutch facings, - Linings
	High alloy steels	**Cutting tools**

APPLICATION CASES

CASE STUDY 1. MEDIUM-LOW DENSITY PARTS

Complex shape PM parts, like water pump pulleys or ABS sensor rings are typically based on FeCuC mixes, at sintered density levels below <6.7g/cm^3.

The main requirement of the component is dimensional stability (inner diameter). The key-feature requested for PM mixes is consistency and enhanced flowability, in order to reduce weight scatter and possibly increase productivity.

- Production trials have been run on water pump pulley
- Servo-Hydraulic presses were utilized with bag-on-press system, in order to optimize mass flow
- Gravity filling method was utilized
- Presses were equipped with weight and compaction force measurement on every individual compacted part
- About 15000 parts per each component were produced

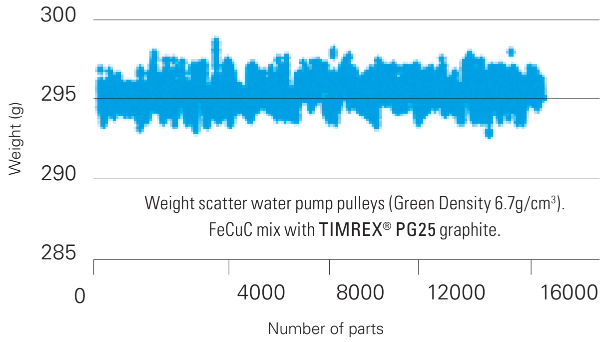
The table summarizes the effective reduction of weight standard deviation obtained simply by shifting from competitor's natural graphite (d90~10µm) to TIMREX® PG25 (d90~ 25µm).

The suggested choice for similar medium-low density PM parts is natural graphite TIMREX® PG25.

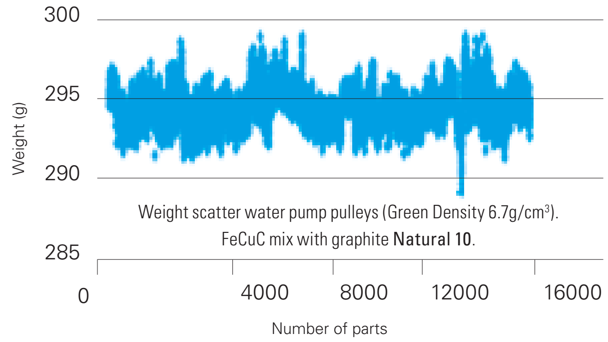
For components requiring particularly tight dimensional specifications, the recommended choice is primary synthetic graphite TIMREX® F25.

GRAPHITE TYPE	TYPE	APRROX. D90 (µm)	AVERAGE PARTS WEIGHT (g)	STD. DEV. (g)
PG 25	Natural	25	295.00	0.77
Natural 10	Natural	10	294.91	0.96

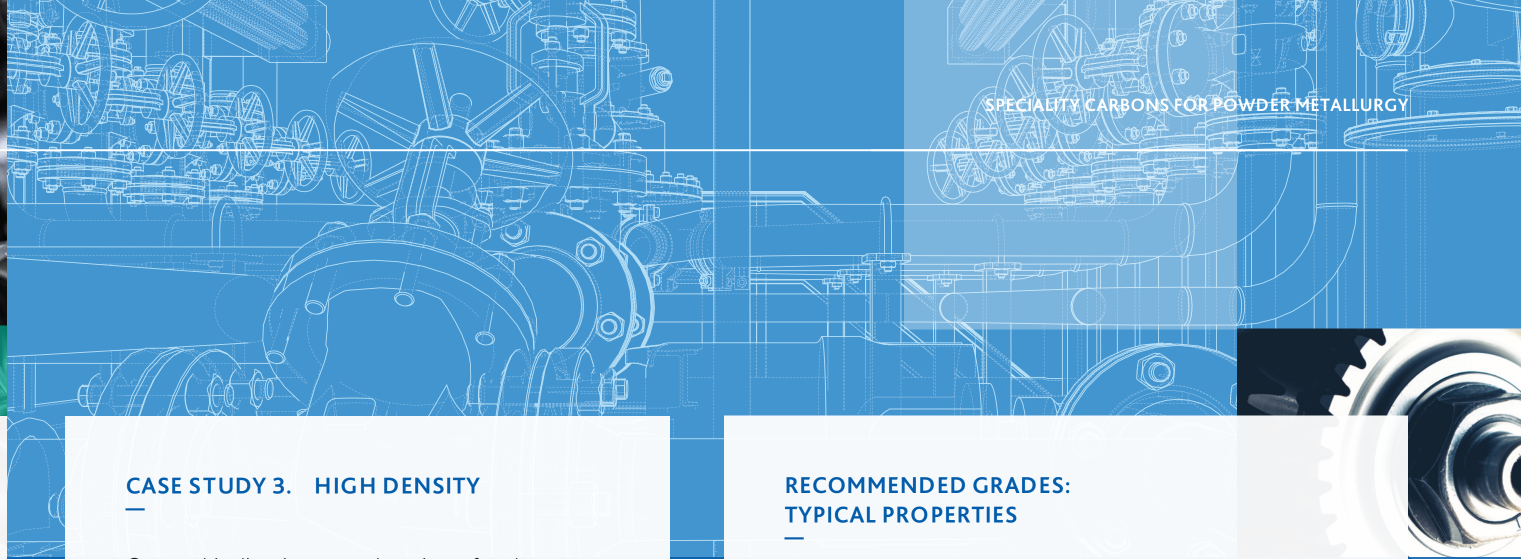
Weight Stability of pressed Water Pump Pulleys. Over 8000 parts production trials.
Powder mixes consisting of Fe +1.5% Cu +0.65% C +0.8% Lubricant



Weight scatter water pump pulleys (Green Density 6.7g/cm^3).
FeCuC mix with **TIMREX® PG25** graphite.



Weight scatter water pump pulleys (Green Density 6.7g/cm^3).
FeCuC mix with graphite **Natural 10**.



CASE STUDY 2. VALVE GUIDES

Graphite plays a double role in this application: Iron matrix hardening as well as friction coefficient modifier, by solid lubrication.

The first function is achieved by efficient diffusion into the original Iron powder particles. It must be pointed out that such components are usually machined after sintering and consequently a certain level of mechanical resistance must be achieved – typically Pearlite is desired as dominant microstructure. Solid lubrication is instead obtained by nondiffused graphite particles that remain within the pores of the microstructure. The selection of graphite powder for this application typically consists of splitting the total required carbon in two selected graphite powders.

Typically a primary synthetic or natural graphite (10µm d90) in the range of 0.5-0.8% is meant to diffuse and reinforce the iron matrix and a coarser graphite powder (44µm d90) is meant to work as solid lubricant [7].

CASE STUDY 3. HIGH DENSITY

General indications can be given for the selection of optimal graphite powder for high performance/high precision PM parts:

- Due to higher reactivity during sintering, primary synthetic graphite **TIMREX® F10, F25, KS44** are the preferred choice when sintering activity and hardenability need to be boosted: this is the case for Cr-alloyed powders, sinter hardening parts, structural components like connecting rods and gears [1, 5, 6, 7].
- When the desired performance is dimensional stability (for instance when weight classes are established for a given PM part production), primary synthetic graphite like **TIMREX® F10, F25, KS44** contribute to the reproducibility of dimensional change values [1, 6].
- Earlier start of sintering process thanks to **TIMREX® F10**, versus natural flakes of similar particles size distribution [5], suggest that sintered cracks or residual tensions in complex-shape PM parts might be reduced by selecting primary synthetic graphite.
- For higher density parts 10µm-d90 is the suggested particles size. Finer particles size. Distributions are suggested only in combination with bonding treatments.

RECOMMENDED GRADES: TYPICAL PROPERTIES

		ASH (%)	CRYSTALLITE HEIGHT Lc (nm)	SCOTT DENSITY (g/cm³)	PARTICLE SIZE DISTRIBUTION d50 (um)	PARTICLE SIZE DISTRIBUTION d90 (um)
SYNTHETIC GRAPHITE	F10	<0.6	80	0.09	6.8	12.6
	F25	<0.6	>90	0.14	11.0	27.2
	KS4	0.07	50	0.07	2.4	4.7
	KS44	0.06	<100	0.19	18.6	45.4
NATURAL GRAPHITE	PG10	3 – 4	>100	0.06	6.4	12.5
	PG25	3 – 4	>200	0.07	10	22
	PG44	3 – 4	>200	0.10	22.4	49.6
CARBON BLACK		ASH (%)	Moisture (as packed) (%)	Pour density (g/cm³)	Suplhur (%)	BET Nitrogen Surface Area (m²/g)
	ENSACO® 250 G	0.01	0.1	0.17	0.02	65

LITERATURE REFERENCES: 1. L. Alzati, R. Gilardi, G. Pozzi, S. Fontana, "Dimensional Consistency and mechanical performance of PM Parts addressed by Graphite TYPE selection", PowderMet2011, San Francisco CA, U.S.A. (2011). 2. D. Edman, L. Alzati, G. Pozzi, C. Frediani, R. Crosa, "Reduced Weight Scatter with Bonded Powder Mixes", World PM2006 Congress, Busan, South Korea (2006). 3. S. Berg, L. Alzati, S. Fontana, G. Pozzi, "Benefits from bonded mixes for complex Powder Metallurgy parts production", EURO PM2007, Toulouse, France (2007). 4. E. Hryha, L. Nyborg, L. Alzati, "Effect of Carbon Source on Oxide Reduction in Cr-Prealloyed PM Steels", World PM2012, Yokohama, Japan (2012). 5. S. St-Laurent, P. Lemieux, S. Pelletier, "Factors affecting the Dimensional Change of Sinter Hardening Powder Grades", PM2TEC Conference, Chicago IL, U.S.A. (2004). 6. S. St-Laurent, E. Ilia, "Improvement of Dimensional Stability of Sinter Hardening Powders under Production Conditions", World PM2010, Florence, Italy (2010). 7. N. Kanezaki, "High Wear and Heat Resistant P/M Valve Guides", Presented at SAE World Congress, Detroit, U.S.A. (2000). 8. A. Lawley, R. Doherty, C. Schade, T. Murphy, "Microstructure and mechanical properties of PM Steels alloyed with Silicon and Vanadium", PowderMet2012, Nashville TN, U.S.A. (2012).

ACKNOWLEDGMENTS: Chalmers University (Sweden), GKN Hoeganaes (U.S.A.), Höganäs AB (Sweden), Metalsinter S.r.l. (Italy) , QMP-Rio Tinto Powders (Canada). Schunk Sintermetalltechnik GmbH (Germany)

IMERYS GRAPHITE & CARBON – A STRONG, INNOVATIVE COMPANY.

With production sites in Europe, Canada and Japan and sales offices in Europe, America and throughout Asia we can ensure security of supply and an optimal customer experience.

OUR EXPERTISE

Imerys Graphite & Carbon is a global company focused on delivering carbon based solutions for manufacturing and industry.

We have over 100 years of experience in the development and production of a wide variety of high quality synthetic and natural graphite powders, conductive carbon blacks, silicon carbide and water based dispersions for various end applications including, but not limited to:

- Lithium-ion Batteries
- Alkaline Batteries
- Lead Acid Batteries
- Fuel Cells
- Conductive Polymers, Plastics and Rubbers
- Carbon Brushes
- Brake Pads and Clutches
- Powder Metallurgy and Hard Metals
- Refractories

Our team of over 500 experienced professionals ensures we deliver optimal solutions for the technical challenges faced by our customers making us the market leader for:

- Conductive carbon blacks and graphites for lithium-ion batteries
- Graphites for alkaline batteries
- Graphites for resin bonded carbon brushes
- Conductive carbon blacks for conductive polymers

IMERYS GROUP

Imerys Graphite & Carbon belongs to Imerys Group, the world leading supplier in mineral based specialties for industry.

The Group draws on its understanding of applications, technological knowledge and expertise in material science to deliver solutions based on beneficiation of its mineral resources, synthetic minerals and formulations. These contribute essential properties to customers’ products and their performance, including heat resistance, hardness, conductivity, opacity, durability, purity, lightness, filtration, absorption and water repellency.

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