



This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No 730871.



Status of C-based materials development and perspectives

1st Workshop of ARIES WP17 PowerMat
27-28 Nov 2017 | Politecnico di Torino, Turin, Italy

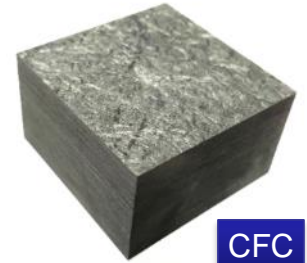
Jorge Guardia-Valenzuela
CERN & University of Zaragoza

Outline

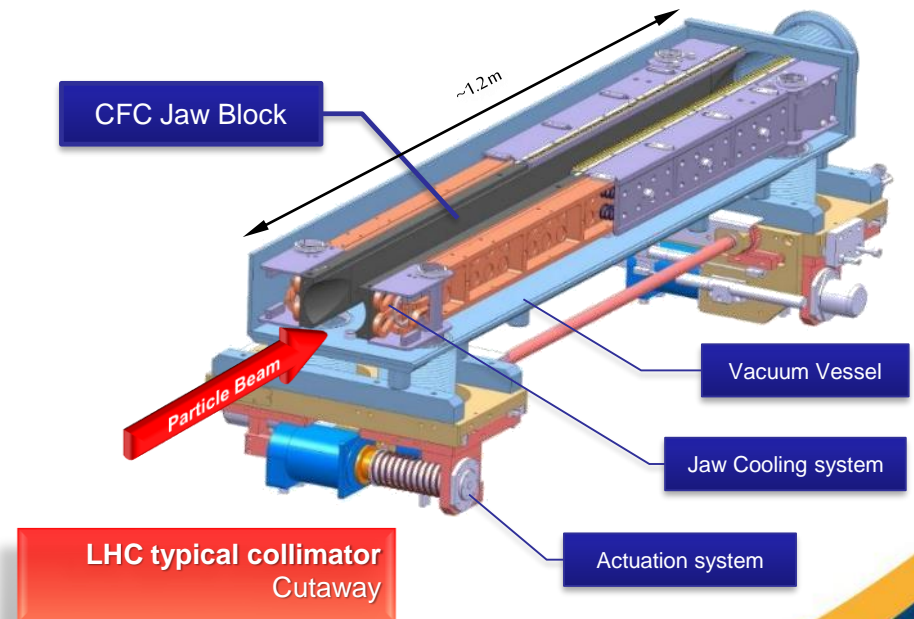
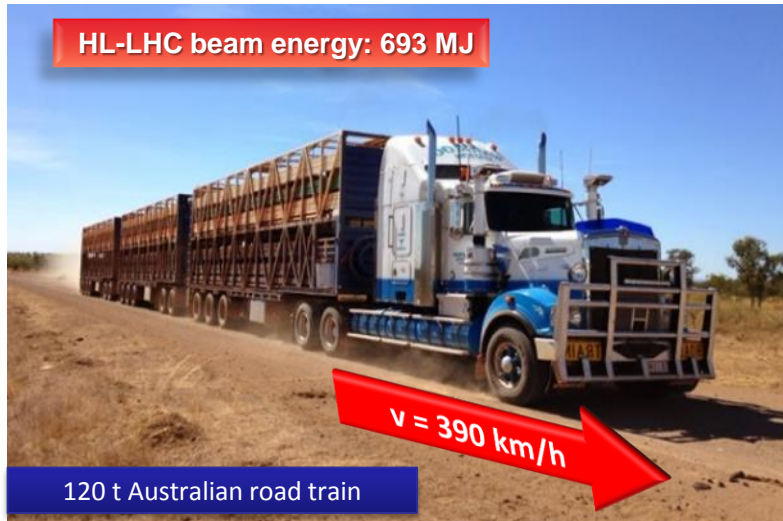
- Introduction
- Molybdenum carbide – graphite
 - Production
 - Role of the structural features in the final use of the material
- Perspectives of graphite-carbide composites
- Other candidate materials
 - HOPG
 - C-Foam

Introduction: LHC Collimation Project at CERN

- The **energy** of the circulating particle beams is equivalent to that needed for melting one ton of copper in few μs **LHC: 362 MJ HL-LHC: 693 MJ**
- Need of a protection system → **Collimators**
- CFC successfully used for LHC baseline but not enough conductive for HL-LHC (resistive wall beam instabilities) → **New graphite-based composite**



CFC

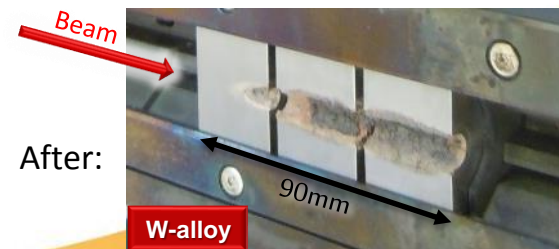
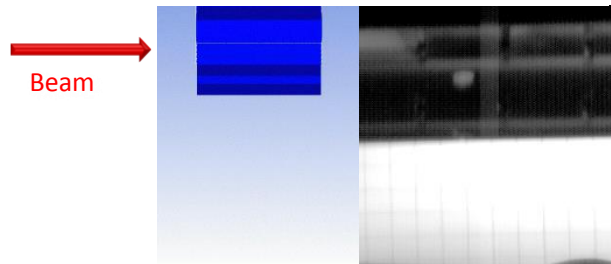


Introduction: Requirements of collimator materials

Extreme environment: thermal shocks (accidental beam impacts), UHV, ionizing radiation, high geometrical stability required...

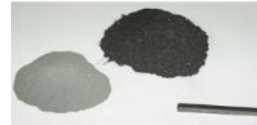
- ↑ **Electrical Conductivity:** limit resistive-wall impedance (beam instabilities)
- ↑ **Thermal Conductivity:** maintain geometrical stability under steady-state thermal loads
- ↓ **CTE:** increase resistance to thermal shock induced by accidental beam impact
- ↑ **Melting/Degradation Temperature:** withstand high temperature
- ↑ **Specific Heat:** improve thermal shock resistance (lowers temperature rise)
- ↑ **Ultimate Strength:** improve thermal shock resistance
- ↔ **Density:** balance to limit peak energy deposition while maintaining adequate cleaning efficiency
- ↑ **Radiation-hardness:** improve component lifetime under long term particle irradiation
- ↓ **Outgassing Rate:** ensure UHV compatibility

**Carbon-based materials have the best compromise of properties: baseline.
Need of higher electrical conductivity → R&D**

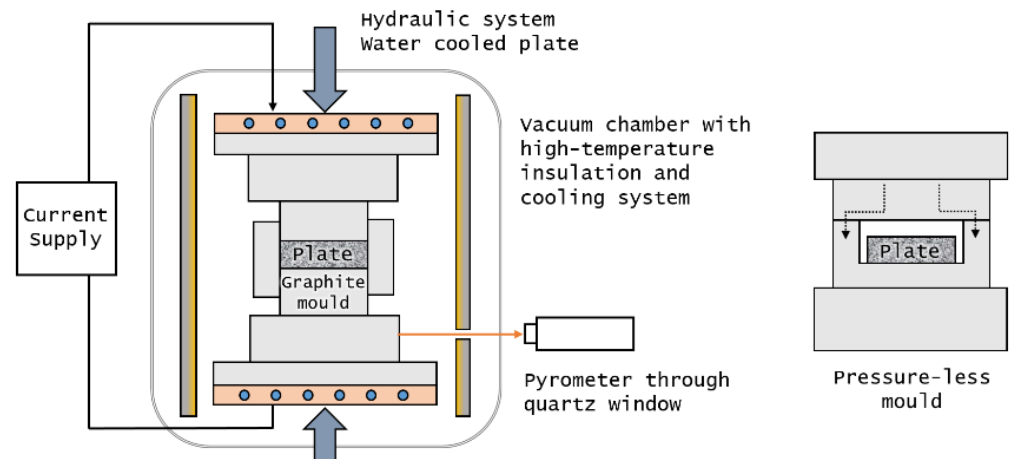
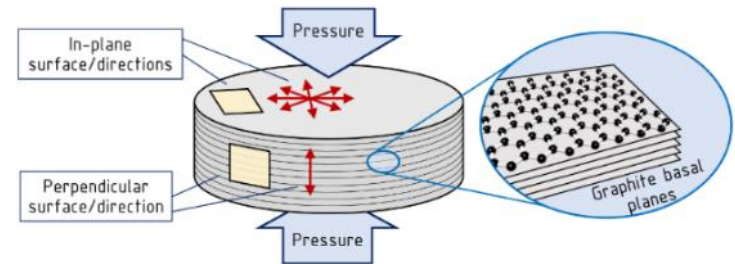
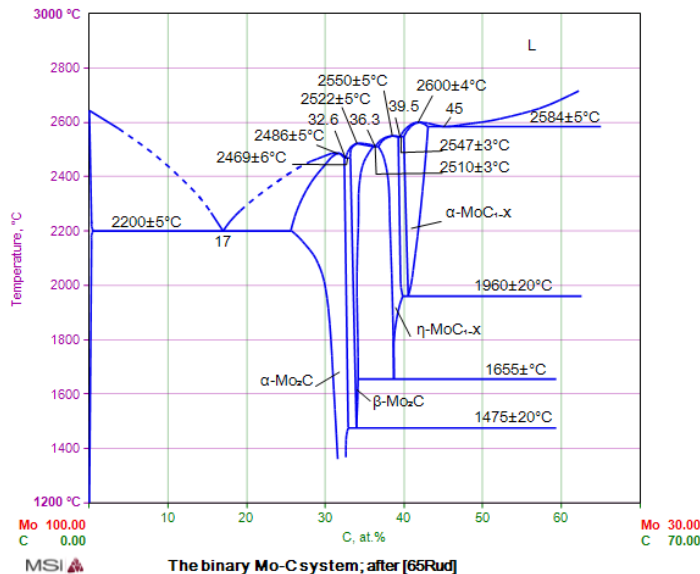
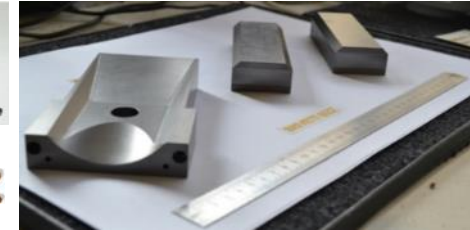


Molybdenum carbide - graphite

- Co-developed with SME Brevetti Bizz (Italy)
- Production: **spark plasma sintering** (SPS)
- Powders of graphite (~90-95vol.%), Mo (~4.5vol.%), CF (0-5vol.%) and Ti
- Melting point of the carbide (~ 2600 °C) reached: **Liquid phase sintering**
- Post-sintering pressure-free thermal treatment: ~2100 °C (under M.P.) or ~2600 °C (above M.P.)



BREVETTI BIZZ

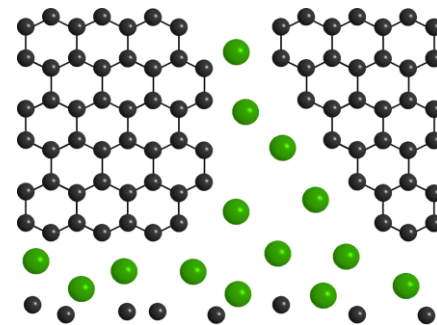


Catalytic graphitization



Catalytic graphitization

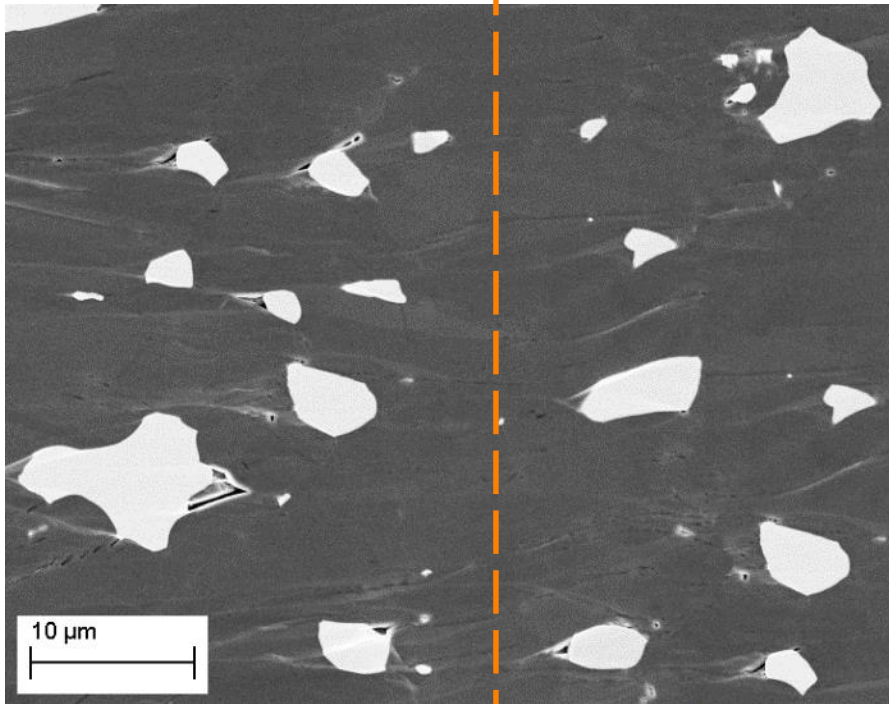
- Use of “**catalytic additions**” to accelerate the process
- **Dissolution-precipitation mechanism**
 1. Carbon dissolution
 2. Carbon diffusion
 3. Precipitation of graphite on active sites
- Grain growth and grain connection
 - Well connected graphite-matrix
 - Orientation of graphite grains
- Carbon fibres appear to be dissolved and re-precipitated
Certain influence in thermophysical properties & radiation hardness



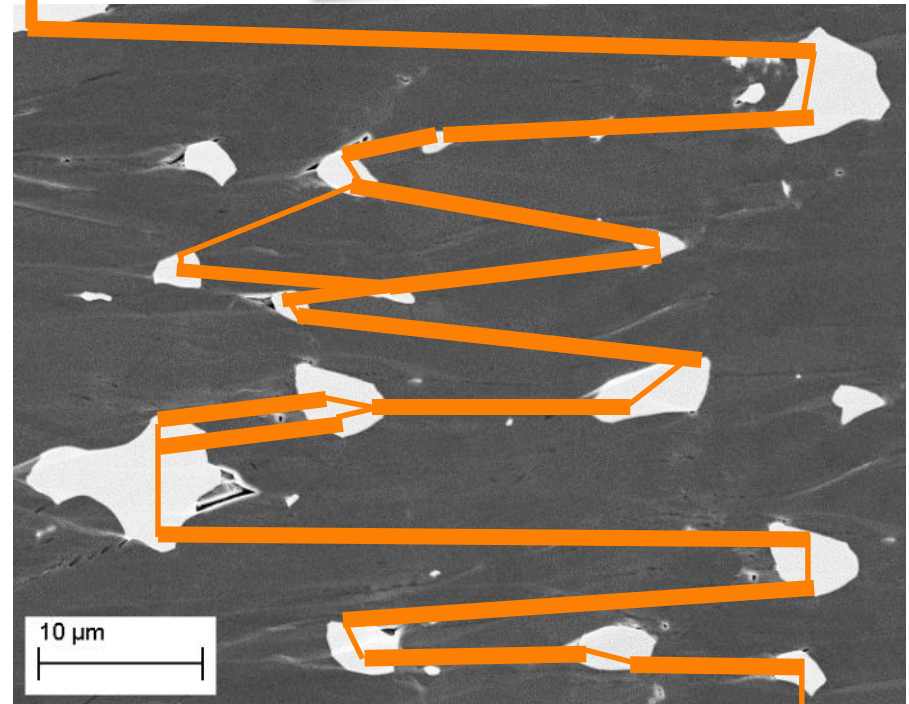
Through-plane reinforcement

T-plane strength also reinforced by the carbide bridges between planes

Sintering pressure direction

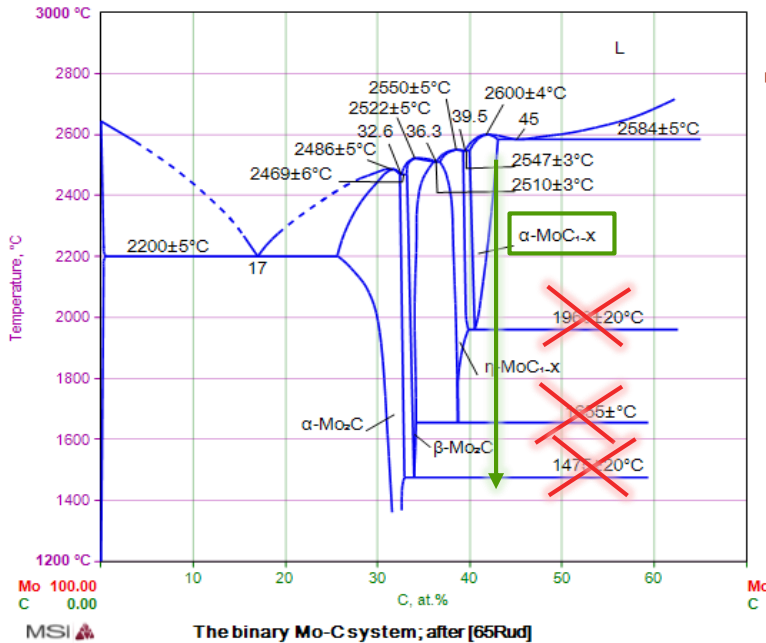


Bad conductivity in the matrix
(Through-graphite planes)

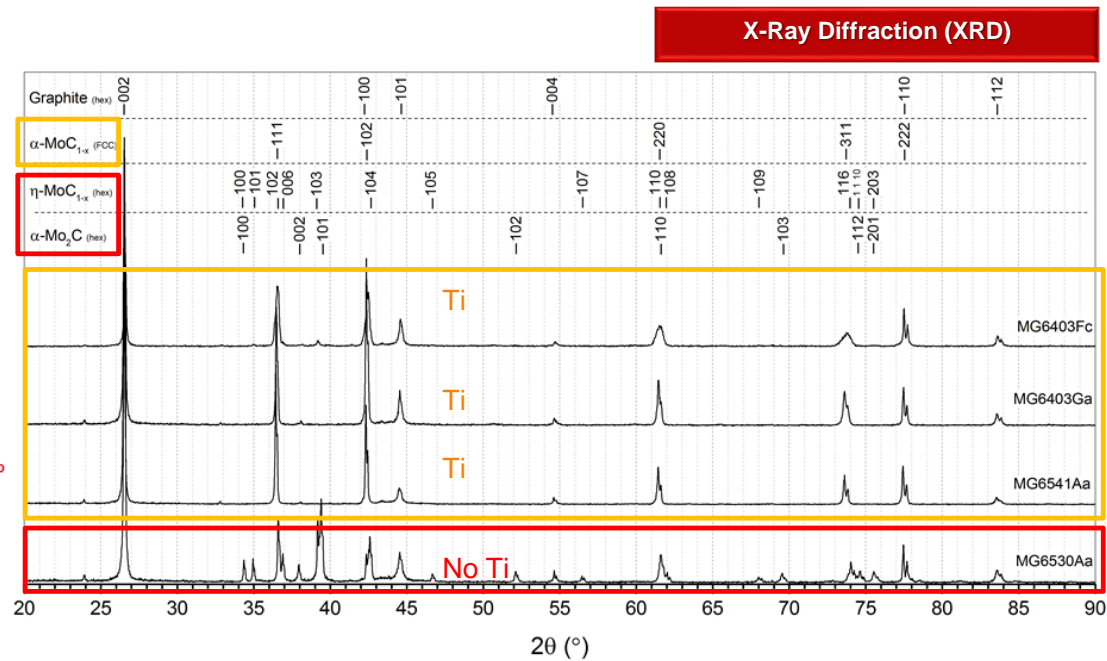


Excellent conductivity along graphite planes.
Carbide particles bridge between planes

Molybdenum carbide phases



- **Titanium doping** $\sim 10\text{Mo}-1\text{Ti}$ (at) $\rightarrow \alpha\text{-MoC}_{1-x}$ phase stabilizer

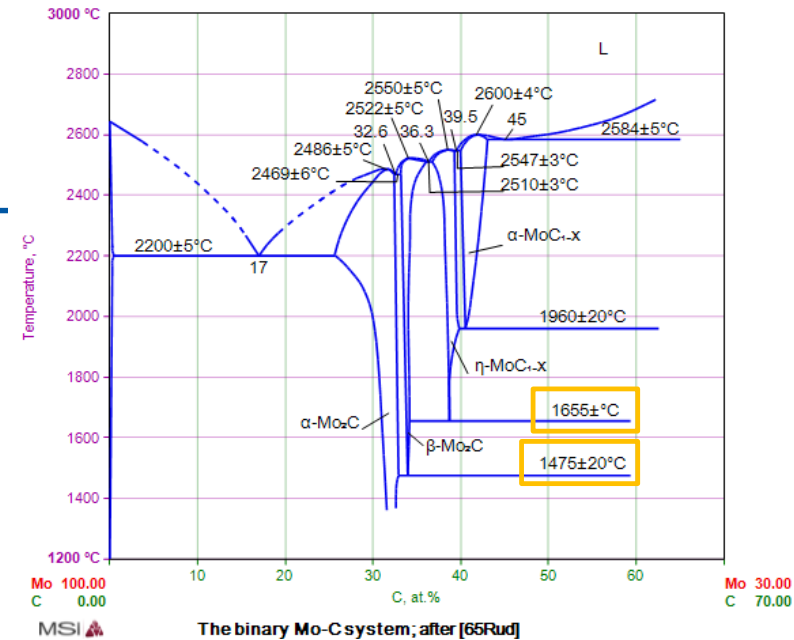


- If **no Ti** is added, there are hexagonal/orthorhombic carbides
- with **Ti** added, there is only FCC carbide (same structure as TiC)
- FCC $\alpha\text{-MoC}_{1-x}$ carbide stable from RT to melting point \rightarrow thermal stability, radiation hardness
- **Graphite matrix** with very high quality. C-spacing: 3.36 Å

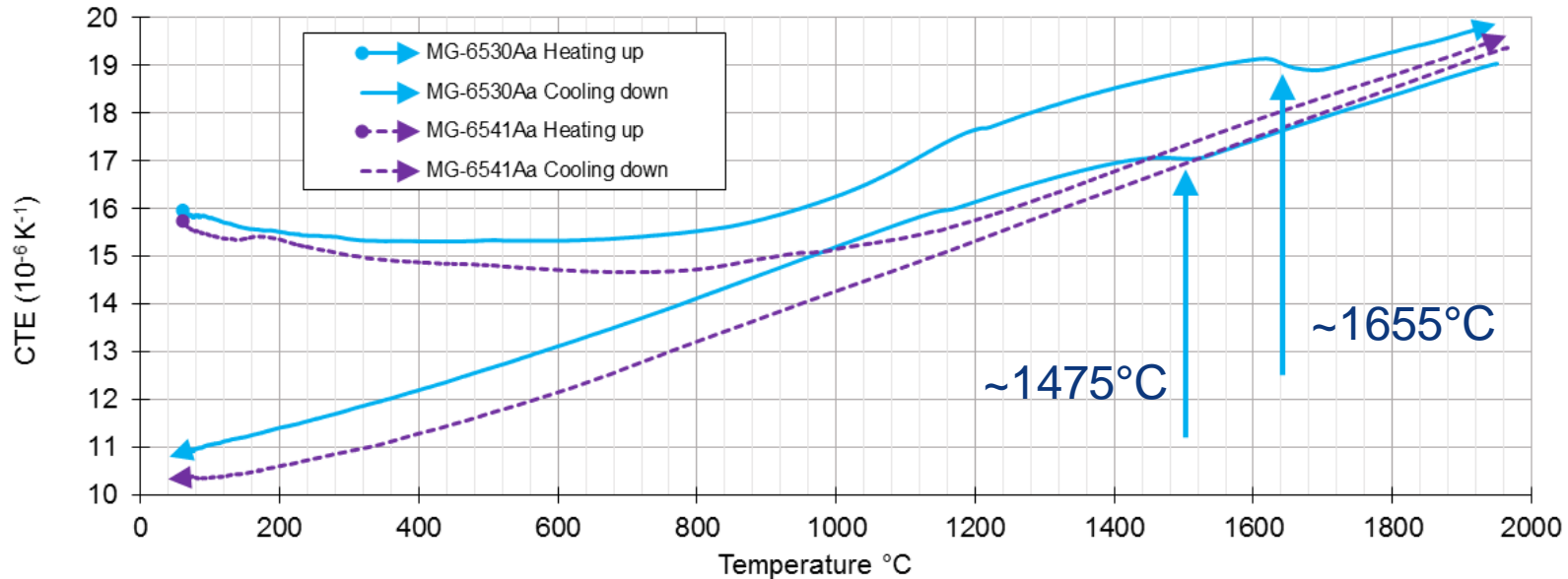
Mo-carbide phase changes

Changes of volume due to phase changes detected in dilatometry measurements.

Risk of cracks during severe thermal excursions (collimator operation)



Perpendicular coefficient of thermal expansion



Mo-carbide cubic carbide

Thermal expansion shows more isotropic behaviour in grades showing the cubic $\alpha\text{-MoC}_{1-x}$ phase, stabilized down to RT by Ti.

Hexagonal carbides have anisotropic CTE. Cubic carbides are isotropic.

CTE Example [10^{-6} K^{-1}]:

- $\eta\text{-MoC}_{1-x}$ (hex): 4.7 (a), 19 (c), measured with XRD *
- TiC (FCC): 7.4

* Acta Metallurgica 36 (8) (1988) 1903 – 1921
doi: 10.1016/0001-6160(88)90293-3.

	MG-6400U	MG-6530Aa	MG-6541Aa	MG-6403Ga	MG-6403Fc	NB-8403Je
Cubic phase	No	No	Yes	Yes	Yes	Partially
CTE 20-1000°C [$\mu\text{m.K}^{-1}$]	1.72	1.74	2.27	2.24	2.95	1.77
⊥ CTE 20-1000°C [$\mu\text{m.K}^{-1}$]	12.94	15.33	13.55	12.49	11.09	15.43
Ratio /⊥	0.13	0.11	0.17	0.18	0.27	0.12

Proposal: Study CTE via X-ray diffraction (XRD) measurements with varying temperature

Advantages: it measures the changes in d-spacing between atomic planes, no matter the orientation in the composite. It measures all directions in one test. Texture could be assessed

Ti addition: catalytic graphitization aid

Grades with Ti have a boost in thermo-mechanical performance.

Specially noticeable in electrical conductivity:

	MG-6400U	MG-6530Aa	MG-6541Aa	MG-6403Ga	MG-6403Fc	NB-8403Je
Ti	No	No	Yes	Yes	Yes	Yes
σ MS/m	0.86	0.83	1.1	0.93	1.01	0.96

Probably due to higher carbon solubility in the molten phase Mo-Ti-C vs Mo-C.
Also higher carbon affinity of Ti vs Mo

	Eutectic Temp [°C]	Eutectic at% C	Eutectic Vol% C (Vol. at RT)	Carbide MP [°C]
Mo-C	~2584	45	31.7	2600
Ti-C	~2740	65	48.1	3084

100% Ti is probably better, but the eutectic Ti-C is even more difficult to reach than Mo-C

Increase graphite grain size & cohesion & minimise defects

- Will Improve in-plane properties, HOPG as reference:

Measured (CERN) electrical conductivity of HOPG (Momentive “TPG”) is 2.5 MS/m. Single layer perfect graphene 100 MS/m, quasi-single crystalline graphite 38.5 MS/m *

Thermal conductivity of HOPG is >1600 W/m/K. Single layer perfect graphene ~5000 W/mK

In-plane CTE RT-1000°C of HOPG is ~0

- Will worsen through-plane properties, HOPG as reference:

Measured (CERN) electrical conductivity of HOPG (Momentive “TPG”) is ~0.0009 MS/m.
Measured (CERN) thermal conductivity of HOPG (Momentive “TPG”) is ~8 W/m/K

- Will affect the stiffness:

Ideal graphite stiffness: In-plane ~1 TPa, Through-plane 36 GPa. Could be problematic for strain-imposed loads (such as thermal loads, while low CTE could improve the situation).

* Igor L. Shabalín. Ultra-High Temperature Materials I. Carbon (Graphene/Graphite) and Refractory Metals. Springer, 2014.

Role of the structural features in the final use of the material

	Act on	Good for	Bad for	Comments
Initial Constituents	Increase graphite grain size, less defects in carbon lattice	+ Thermal and elec. conductivity	- Strength	Foreseen test
	Reduce carbide grain size	+ Strength Probably easier to machine	- Through-plane properties	Current size ~5 μ m
	Metal content	+ Electrical and thermal conductivities - Through-plane CTE + Strength	- Specific heat. + Density + In-plane CTE	Already optimized: +Performance -Energy deposition
	Phase stability	Avoid changes of volume due to phase changes (cracks)	-	Ti addition provides stabilized cubic carbide (both). Content to be studied
	Cubic carbide	+ Isotropic CTE. (Easier XRD analyses)	- Harder (machining)	
	Carbon fibres	+ mechanical properties - Radiation swelling	-	GSI irradiation tests
Processing (sintering)	Increase graphite texture	+ In-plane properties	- Through-plane properties	Foreseen test
	Porosity	+ Accommodation of internal stresses? - Radiation swelling? - Outgassing?	- Thermo-mechanical properties	
	Improve graphite grains cohesion	+ Strength + Thermal and elec. conductivity	+ Stiffness	Foreseen test

Graphite-carbide composites perspectives

- Tests of new carbide-graphite material grades
 - Binder pitch
 - Big graphite flakes
 - Carbon black
- HOPG
- C-Foam

Test with binder pitch

Used in graphite/CFC industry as binder.
It will help to bond graphite crystals together

It decomposes volatile compounds and those in hydrogen.
Use small volumes

The decomposition produces gas and volume reduction.
For graphite manufacturing, the bodies are heat-treated to carbonise the pitch (no pressure) in order to degas slowly (hours-days). The final product is porous, then is densified. Different approach.



For a plate 150x100x30 mm, if 20 vol% pitch is used:
Carbon yield 70%, initial density 1.2 g/cm³
Final density carbonised pitch ~2 g/cm³.
Volatiles average at. Mass~ 60 g/mol
(anthracene C₁₄H₁₀, pyrene C₁₆H₁₀, methane CH₄...)

Volatiles produced: 0.1 L

Average increase of pressure on the plate: 6.5 MPa (35 to 41.5 MPa)

Volatiles will decompose in carbon and **hydrogen (around 0.03 L)**

Hydrogen can diffuse out from the plate and mould at high temperature.



Test with “big” graphite flakes

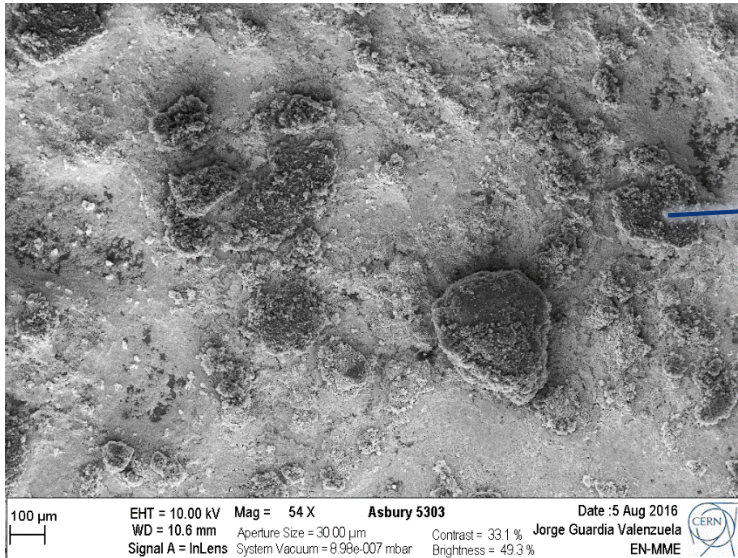


Asbury 3763
High-purity natural-graphite flat-flakes
Diameter ~1 mm
Few defects from production (few milling steps)

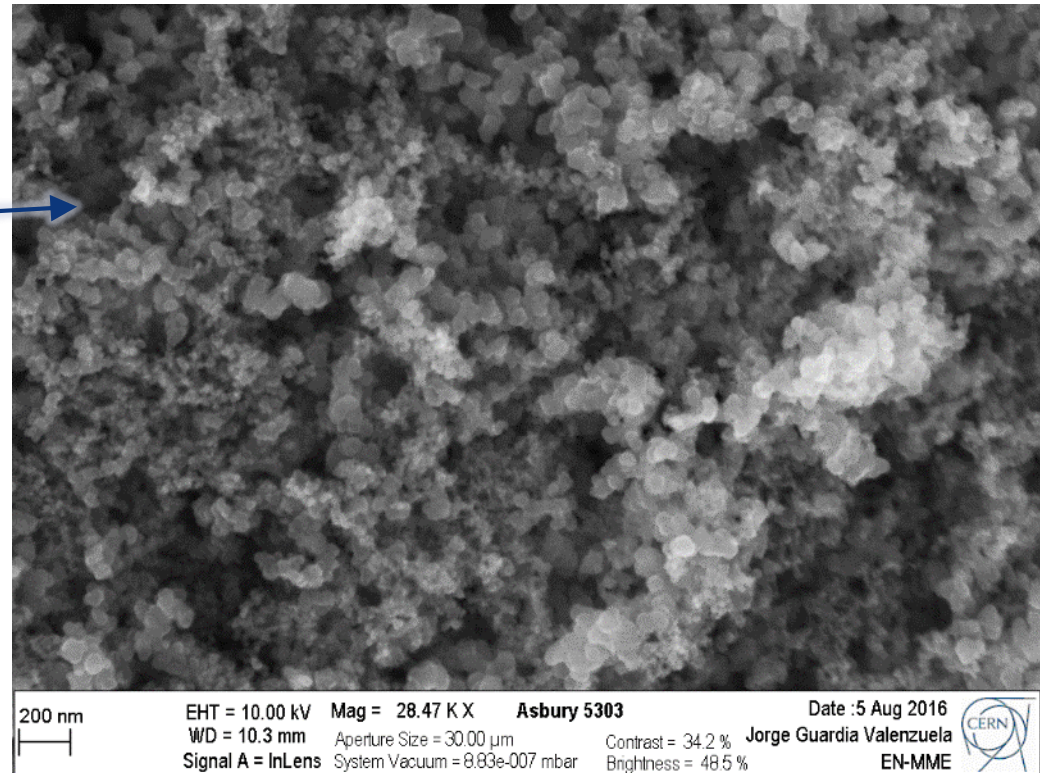
Goals:

- In-plane properties will improve (thermal-electrical conductivities). Best initial conditions for this.
- Check how much the transversal properties will worsen
- Check how is the strength

Test with carbon black



Asbury 5303
High-purity carbon black
Diameter 50-100 nm
Smallest possible carbon powder



Goals:

- Study full graphitization of the initial carbon content, with complete initial isotropy.
- Study the connection of graphite grains during sintering
- Straightforward to compact (spheres, no flat flakes)
- Study vacuum behaviour
- Check final properties. Extent of graphitization?

HOPG (Thermal pyrolytic graphite “TPG”)

Produced by CVD from methane gas. Usually is annealed at graphitizing temperatures ($\sim 3000^{\circ}\text{C}$), with or without strain. Is a “thick” coating. Thickness limitation around 15mm. Typical size up to 300x100 mm

Price per volume unit increases with thickness: ~ 100 USD 250x8x7 mm (1 HRMT36 bar). ~ 150 USD 30x30x10 mm

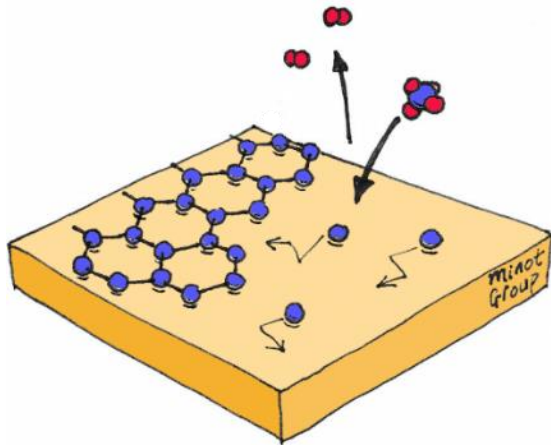


Image credit: “Minot Group, Oregon State University”



HRMT36 bars came slightly bent (~ 1 mm Sagitta in 250 mm). Probably due to thermal stresses during production



HOPG

Excellent in-plane properties. Electrical conductor material with the highest thermal conductivity

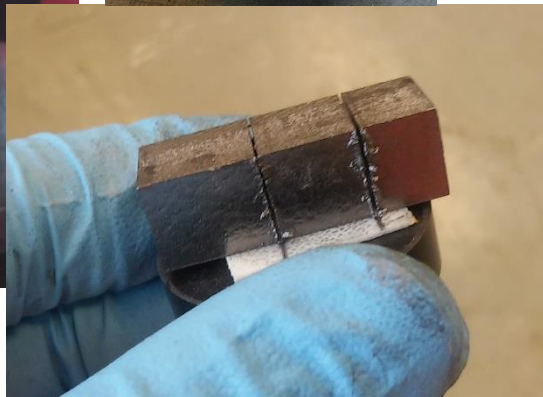
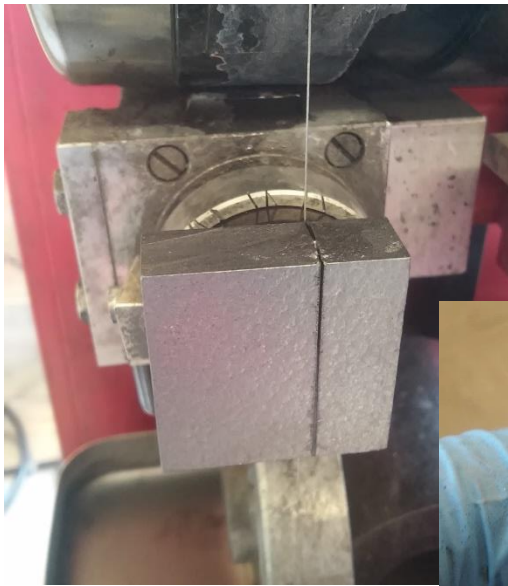
Very weak (mechanically) in through-plane direction.

Needs some special care with machining: the company advised not to machine the in-plane surface

No problems to cut it (diamond wire) if careful with bending stresses

Delaminates very easily if weak direction is stressed. Peeling off some glue only removes a very thin layer of material

Transversal surfaces are very easy to mirror polish. In-plane surface not tested yet

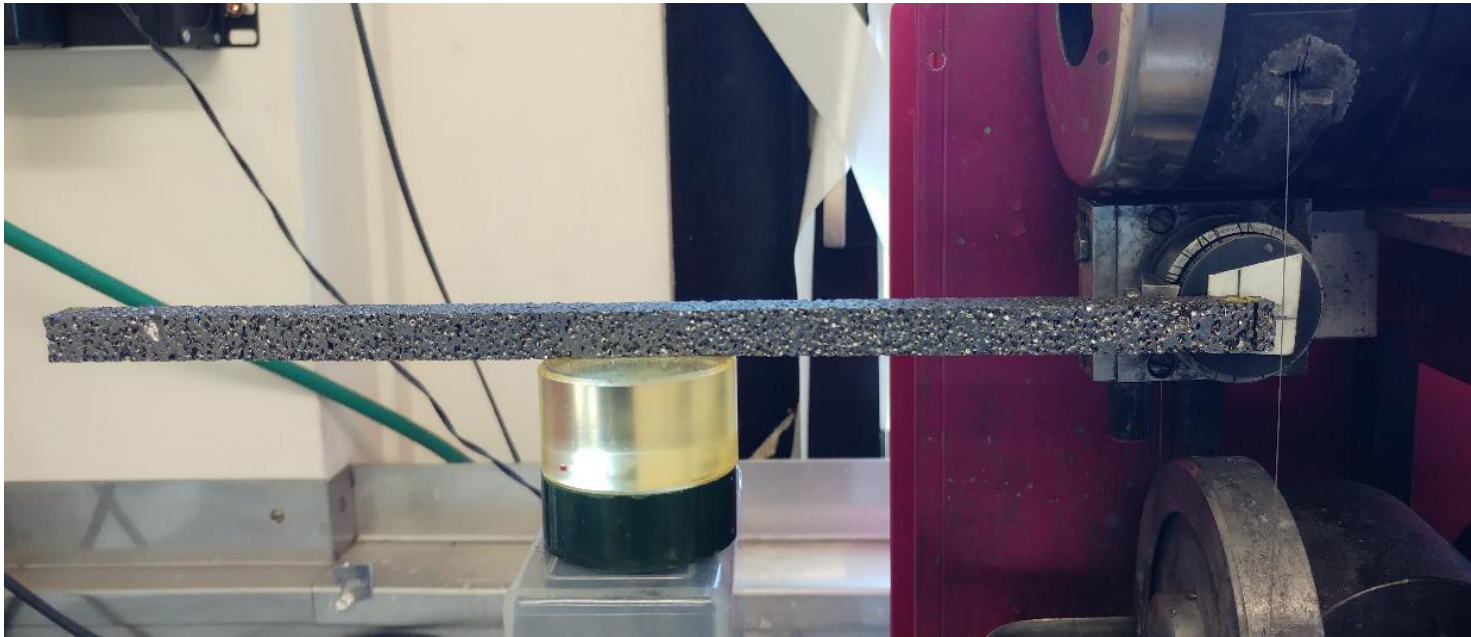


C-Foam

Produced by a US company, spin off from Oak Ridge National Laboratory
Profits from volatiles generated during carbonization of pitch to form bubbles → pores
Very low density $\sim 0.4 \text{ g/cm}^3$ → FCC collimator absorber candidate
Highly graphitized pore walls (3D graphite network) → High thermal conductivity

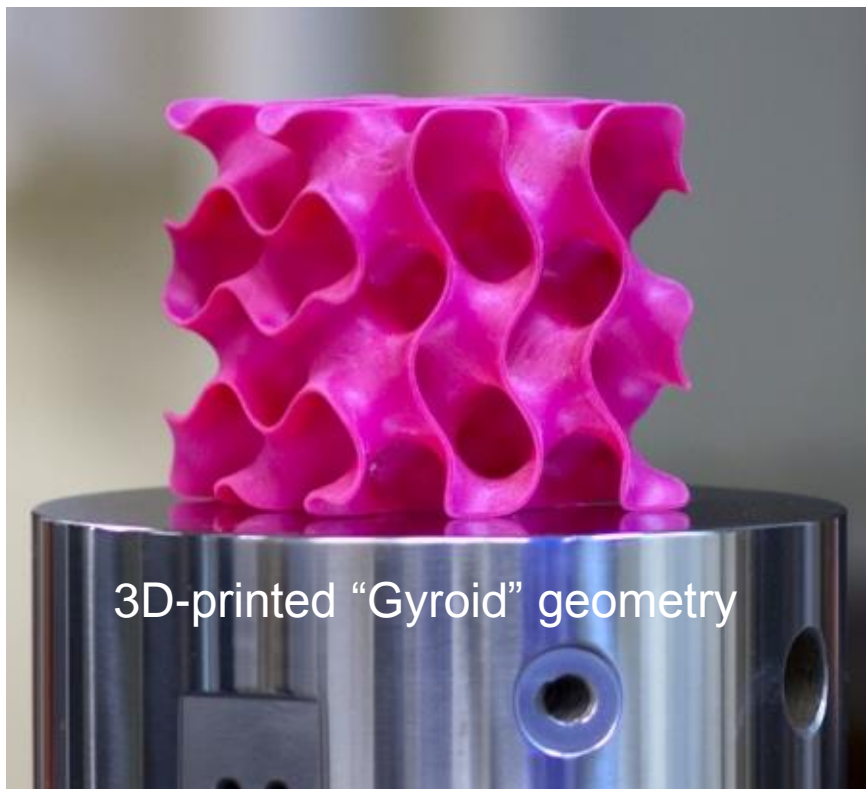
Tends to keep a lot of graphite dust from machining in the pores:
Difficult cleaning (vacuum cleaner is the most effective)
Ultrasound bath seems not to damage the structure

Easy to machine
Breaks easily if is impacted or bent.



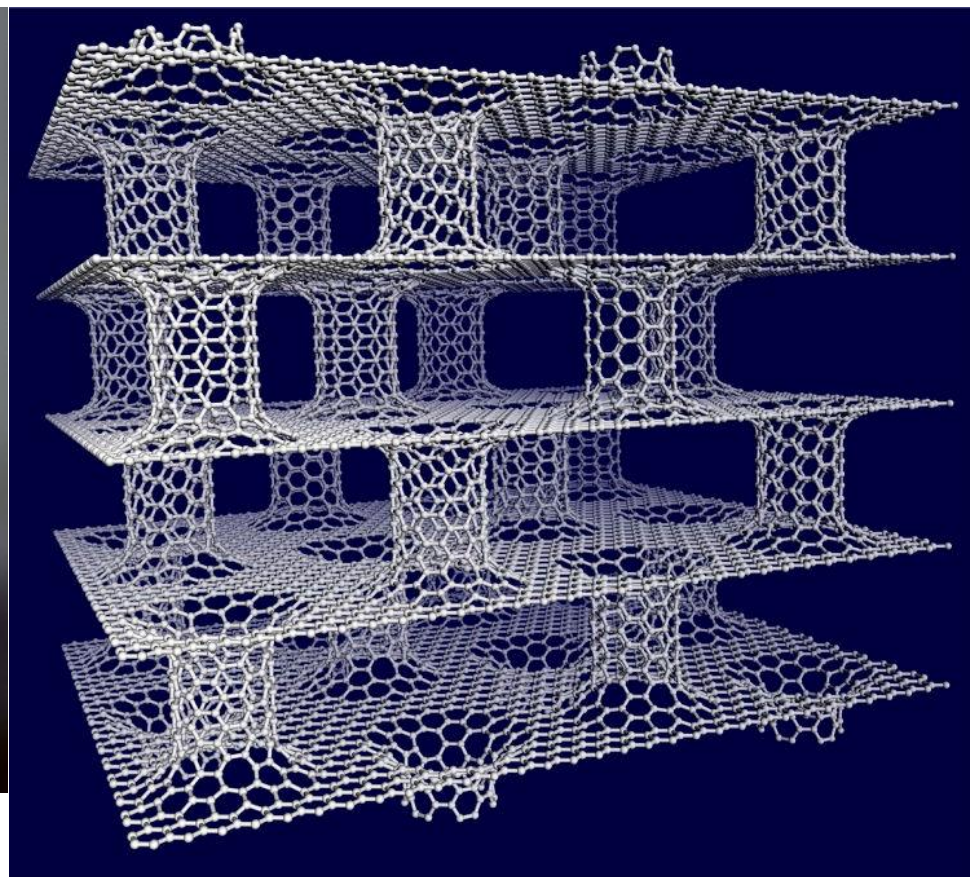
Future challenges in graphene-based materials

Translate 2D advantages of graphene/HOPG into 3D materials



3D-printed “Gyroid” geometry

Science Advances 06 Jan 2017:
Vol. 3, no. 1, e1601536
DOI: [10.1126/sciadv.1601536](https://doi.org/10.1126/sciadv.1601536)



Graphene-nanotube hybrid



Thank you for your attention!



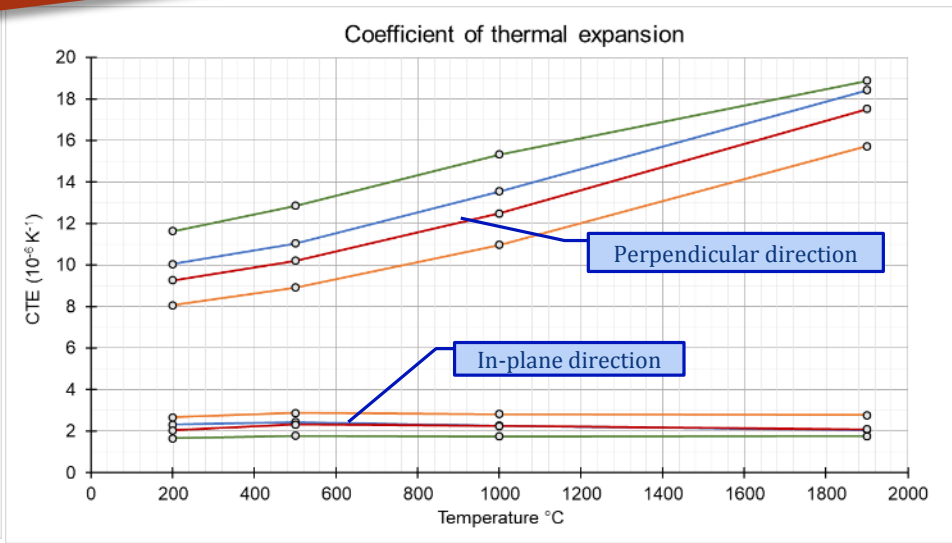
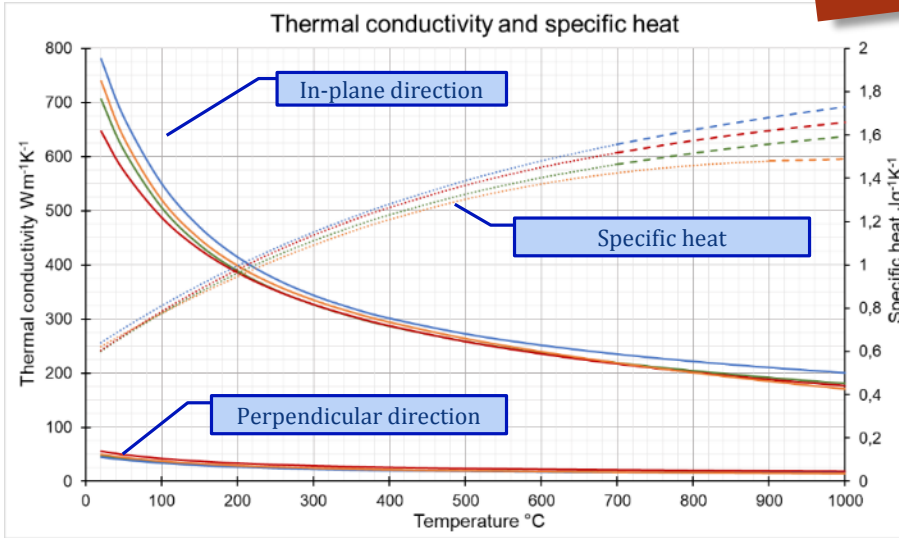
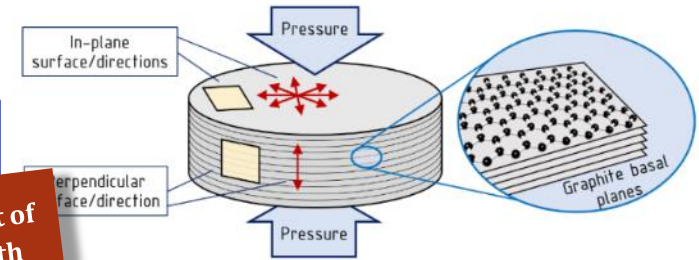
Backup slides



Typical MoGr properties

	In-plane	Perpendicular	
Electrical conductivity [MS/m]	~1	~0.08	10-15x isotropic graphite
Thermal Conductivity [W/(mK)]	700 - 800	~50	2x Cu
CTE RT ÷ 200 °C [$10^{-6}K^{-1}$]	1.7 - 2.7	8 - 12	~ isotropic graphite
Flexural Strength [MPa]	60 - 80	10 - 12	
Specific Heat [J/(gK)]		0.6 - 0.65	
Density [g/cm ³]	Al	2.5 - 2.6	

Carbides: Improvement of the weak direction with respect to HOPG



Rhombohedral-hexagonal transformation

ξ -Mo₂C carbide is orthorhombic, with Mo sub-lattice being hexagonal. XRD shows hexagonal structure when using X-rays (Cu) because they hardly “see” the carbon atoms. Neutron diffraction is more appropriate to distinguish the orthorhombic structure.

E. Parthé, V. Sadagopan, The structure of dimolybdenum carbide by neutron diffraction technique, Acta Crystallographica 16 (3) (1963) 202–205. doi:10.1107/S0365110X63000487.

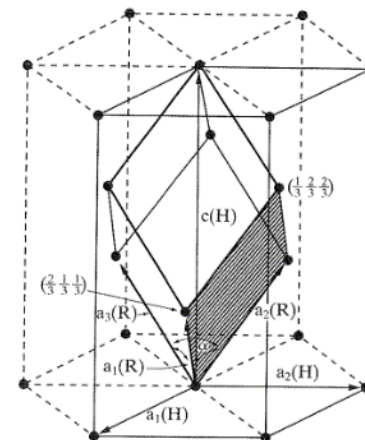
$$a_{orth} = c_{hex}$$

$$b_{orth} = 2 \cdot a_{hex}$$

$$c_{orth} = \sqrt{3} \cdot a_{hex}$$

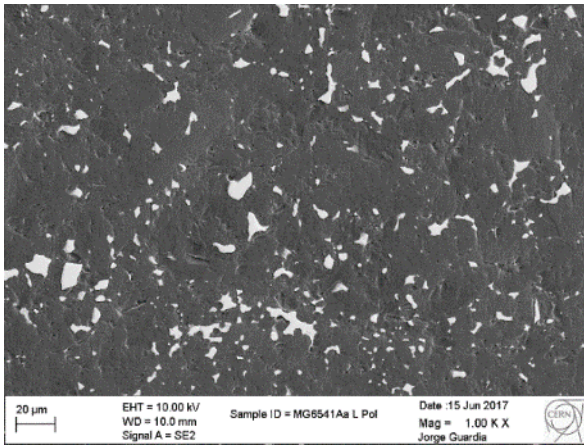
	Structure	Lattice parameters (Å)
<i>Mo</i> ₂ <i>C</i> (ζ -type) ¹	Orthorhombic	$a = 4.739$ $b = 6.024$ $c = 5.215$
<i>Mo</i> ₂ <i>C</i> (ϵ -type) ¹	Hexagonal	$a = 3.010$ $c = 4.735$

Figure A4-1 Rhombohedral and hexagonal unit cell in a rhombohedral lattice.



Microstructure

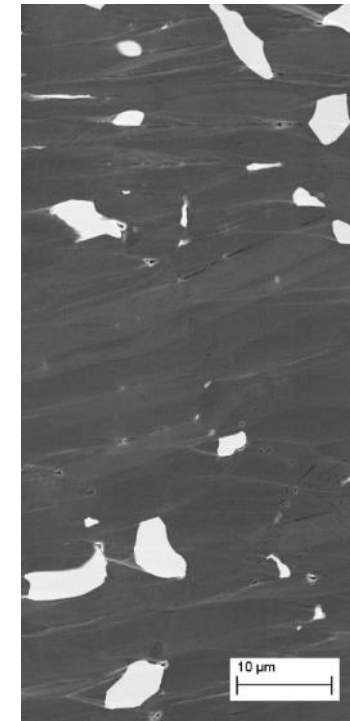
Sintering pressure direction



In-plane polished surface



Perpendicular fracture surface



Perpendicular ion-polished surface

- Carbides: $\sim 5 \mu\text{m}$ diameter
- Well-connected graphite matrix
- Well-compacted: porosity $< 0.5 \text{ vol.}\%$
- Molybdenum carbide particles reinforce the graphite, holding together the graphite in the weak direction

