I.FAST

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DELIVERABLE REPORT

Evaluation of a Carbide-Carbon Material (CCM) alternative to Molybdenum-Graphite

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ABSTRACT

Carbide-Carbon Materials (CCM) are a family of composites of wide interest for use in HEP facilities and, thanks to their high thermal conductivity and low density, they are very promising in several fields of the industry, including thermal management applications, aerospace, nuclear energy production. However, the high production costs are limiting, so far, their application for big series productions. There are two ways, investigated within WP4, for an effective cost reduction: the first one is related to the increase of the material volume produced in each machine cycle. The second way involves a decrease of the production temperature, thus reducing the energy consumed during the cycle, as well as decreasing the consumption of elements such as moulds and electrodes. Work within WP4 is advancing in both directions and this milestone focuses on the second aspect, which concerns the identification of a CCM with lower sintering temperature than the Molybdenum-Graphite (MoGr) produced by Nanoker and used in HL-LHC secondary collimators.

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Executive summary

This milestone describes the identification of a Carbide-Carbon Material (CCM) with significantly lower production temperature than the Molybdenum-Graphite (MoGr) commercially produced by Nanoker, which is the IFAST WP4.4 industrial partner.

The first section of the document gives an introduction to CCM, and highlights the main contributors to the high production cost. It also gives a tentative expected cost reduction when reducing the sintering temperature from ~2600 °C to 2000 °C or less, and when increasing by a factor of 2 the size of the material volume produced at each cycle.

The second section reports the technical specification defined for the CCM in the scope of WP4.4. This specification has been defined based on the needs for HEP elements such as the HL-LHC collimators; however, the high thermal properties, mechanical strength and low density, are required in several types of industrial applications. The chapter also reports the properties of the MoGr, which is the baseline for the WP4.4 activity, and compares them to the requirements of the technical specification. These are the targets that shall be matched (or exceeded) by an alternative material produced at lower temperature.

The third section describes the identification of a MoGr alternative that can be sintered at 2000 °C ore less. This, compared to the 2600 °C sintering temperature of MoGr, has a very positive effect on the energy used per cycle, with a corresponding reduction of cost. Moreover, this temperature reduction allows saving expensive elements of the machine, such as mould and electrodes, which need to be changed at each cycle when producing MoGr, leading to a further cost reduction. The identified material is Chromium-Graphite (CrGr). The section documents the several production runs completed on small testing plates, to optimize the composition and the other cycle parameters. We report and describe here also the large-scale plates produced with the optimized composition.

The fourth section describes the thermophysical characterization performed on CrGr at CERN, in the Mechanical Laboratory of the Engineering Department. It also reports the results and compares MoGr to the requirements of the technical specification and to MoGr properties, showing that CrGr is a promising alternative that deserves further optimization in the next years of the project.

The last section of the document summarizes the main results and show the future plans for the optimization of the material.

1 Introduction

The objective of WP4.4 is to develop and industrialize materials with low density and high thermal, mechanical and electrical properties. A technical specification has been drafted at the beginning of the project, to define the minimum thresholds of properties of the materials, which is produced at Nanoker (ES). A material that would fit with such properties is Molybdenum-Graphite (MoGr) [1], a Carbide-Carbon Material (CCM) already successfully developed within previous European projects such as ARIES (WP14 & WP17) [2], and industrially produced and installed in LHC secondary collimators in 2018/20. Such material is very promising for industrial application, but a wide use of it is hindered by the production costs. On way of limiting the cost is increasing the amount of material produced in each sintering cycle. When increasing the sintered volume, the increase of energy spent for the process is modest or, in some case, negligible, such that the cost per unit volume of the material goes down. A second way of reducing costs is identifying a lower-temperature sintering material. This leads to a lower energy spent for the process, and on top of that it allows saving parts of the mould and electrodes which would be otherwise consumable in higher-temperature sintering materials such as MoGr. This MS focuses on this second aspect, proposing and validating an alternative, cheaper solution to MoGr.

As a starting point in the identification of an alternative material to MoGr, WP4.4 focused on Chromium-Graphite (CrGr) [3]. Chromium carbide possesses a lower melting temperature with respect to molybdenum carbide, allowing a liquid-phase sintering at temperatures equal or lower than 2000 °C, compared to MoGr which requires a sintering temperature of 2640 °C, a more demanding insulation system and a higher need of power, leading to a quick deterioration of the machine elements. First essays with the sintering of CrGr were done at Brevetti Bizz during ARIES, WP14 and WP17 [4]; the material was promising on the thermal point of view, but extremely low in mechanical strength, presenting a maximum bending strength in the order of 10 MPa in the base plane directions. Such a low mechanical strength, on top of restricting the possible use of the material to applications with little to no applied mechanical stress, also prevents an effective machining of the material, as it easily breaks during this operation. Scope of the work during the first year of IFAST WP4.4 was to improve the mechanical properties of the material by at least a factor of 5, to prove its possible use as a valid, cheaper alternative to MoGr.

Table 1 gives a qualitative estimation on the possible cost reduction for different options of produced volume and material type.

Table 1. Qualitative estimation of cost reduction for different options of produced materials and sizes.

Material	**Plate size**	**N. plates produced in the same cycle**	**Normalized Price***
MoGr	Ø170 mm	2	100%
MoGr	Ø230 mm	2	~90 %
CrGr	Ø170 mm	2	~80 %
CrGr	Ø230 mm	2	~70 %

* *Estimation for an industrial production of at least 50 plates, including fine machining. To be confirmed after testing.*

2 CCM technical specification

At the beginning of the project, CERN defined a technical specification identifying the minimum properties requested to the material under development. This specification, reported in Table 2, is based on the needs of beam-intercepting devices such as HL-LHC collimators; however, this set of properties is very desirable also for other high-end applications and domains, such as thermal management, aerospace, nuclear energy production, accelerator-driven systems.

Table 2. Minimum required thermophysical properties for the material developed in the scope of WP4.4.

Property	∥*	⊥	Unit
Density at 20ºC	2.40 – 2.60		[g/cm³]
Specific heat at 20ºC	> 0.6		[J/(g·K)]
Electrical conductivity at 20ºC	> 0.75		[MS/m]
Thermal Diffusivity 20ºC / 300ºC	> 350/100	> 20/6	[mm²/s]
Thermal conductivity at 20ºC / 300ºC	> 500/280	> 35/20	[W/(m·K)]
Volumetric CTE 20-1000ºC	< 7		[$10^{-6}K^{-1}$]
Coefficient of thermal expansion 20-1000ºC	< 2.9	< 15	[$10^{-6}K^{-1}$]
Young's Modulus at 20ºC	35 < E < 75	5 < E < 8	[GPa]
Flexural strength at 20ºC	> 60	> 10	[MPa]
Flexural strain to rupture at 20ºC	> 2500	> 4000	[µm/m]
Dimensional stability*	< 0.05	< 0.25	%

**The dimensional stability shall be ensured after the following thermal cycle: heating of the specimen up to 1950ºC with a ramp of 5ºC/min. Cooling of the specimen down to room temperature with the same ramp.*

3 Chromium-Graphite production runs

Nanoker and CERN initially defined a set of parameters in terms of material composition, green pressure, sintering temperature, pressure and dwell time, in order to evaluate the best combination for chromium-graphite. Given the high number of trials necessary, this initial optimization process was run in the smaller of the two SPS machines available at Nanoker, on small disks of Ø60 mm, to maintain the production cost and time low. Results in terms of material compaction and electrical conductivity, for the different tested combinations, are reported in Table 3.

Table 3. Determination of CrGr optimal production parameters, with tests on Ø60 mm plates.

Test	Green		Sintering			Initial composition							
	Pressure [MPa]	Density [g/cm3]	Sintering T [°C]	Sintering time [s]	Sintering P [MPa]	Cr3C2 vol%	Cr vol%	Eq. Cr2C3 vol%	Ti vol%	CF cytec vol%	Gr 93004 vol%	Density [g/cm3]	El. Conductivity [MS/m]
1	42	1.367	2000	1200	25	1.9	0	-	0	5.8	92.3	1.367	0.07
2	42	1.43	2000	1200	25	1.9	0	-	0	5.8	92.3	-	0.07
3	42	1.26	2000	1200	25	1.9	0	-	0	5.8	92.3	-	0.09
4	10.5	1.25	2100	1200	25	1.9	0	-	0	5.8	92.3	1.78	0.07
5	10.5	-	2100	1200	25	0	5.5	6.9	0.6	0	93.9	2.29	0.78
6	10.5	1.52	2100	1200	25	0	10	12.7	0.6	0	89.4	2.34	0.94
7	10.5	1.58	2100	1200	25	15	0	-	1	5	79	2.4	1.04
8	10.5	1.53	2100	1200	25	15	0	-	0	5	80	2.41	1.15
9	10.5	1.57	2000	1200	25	15	0	-	1	5	79	2.41	1.04
10	10.5	1.55	1900	1200	25	15	0	-	0	5	80	2.39	1.12

Based on the results, the best compromise was found with plate #9. Plate #8 shows even better conductivity, but the higher temperature is detrimental in terms of energy consumption and degradation of the machine elements. Plate #10 is also promising, but it showed a worse compaction. Anyways, these last three plates were used as a base for an upscaling of the plate size, and a sintering in the bigger of the two SPS machines at Nanoker of Ø170 mm plates.

Figure 1 – Nanoker large-size SPS machine.

Good results were achieved by Nanoker with two successive production runs, at a sintering temperature of 2000 °C maintained for 20 minutes under a 20 MPa pressure, and followed by an annealing treatment at 1700 °C for 3 hours. The difference between the two runs was the machine configuration: in the first run, a single Ø170 mm disk was sintered. In the second run, the machine configuration consisted in two Ø170 mm disks positioned one above the other, in series with respect to the electric current flow, which generates heating by Joule effect. Results of the two runs are summarized in Table 4.

Table 4. Density and electrical conductivity of the Ø170 mm plates sintered by Nanoker in two successive runs in the large-size SPS machine.

Sintering Run	Plate number	Density (g/cm3)	Electrical Conductivity (MS/m)
#1	**Plate #1**	**2.30**	**1,00 – 1,07**
#2	**Plate #2**	**2.23**	**0.75 – 0.76**
	Plate #3	**2.29**	**0.80 – 0.81**

Moving to a double-plate cycle, so far, does not allow yet achieving a compaction level and properties comparable to the single-plate cycle. The machine parameters and the composition must be tuned to allow going up in sintered volume of CrGr in each cycle.

4 Chromium-Graphite characterization and results

The promising results in terms of electrical conductivity of the first run of CrGr, with Ø170 mm plate, are an indication of good material sintering and compaction. It was thus decided to perform a full thermophysical campaign of measurements at CERN, to compare the full set of properties with the technical specification. All the tests were performed in the EN-MME Mechanical Laboratory at CERN, with advanced instrumentations allowing to monitor the material properties over a wide range of temperatures. The main results are shown in the figures below.

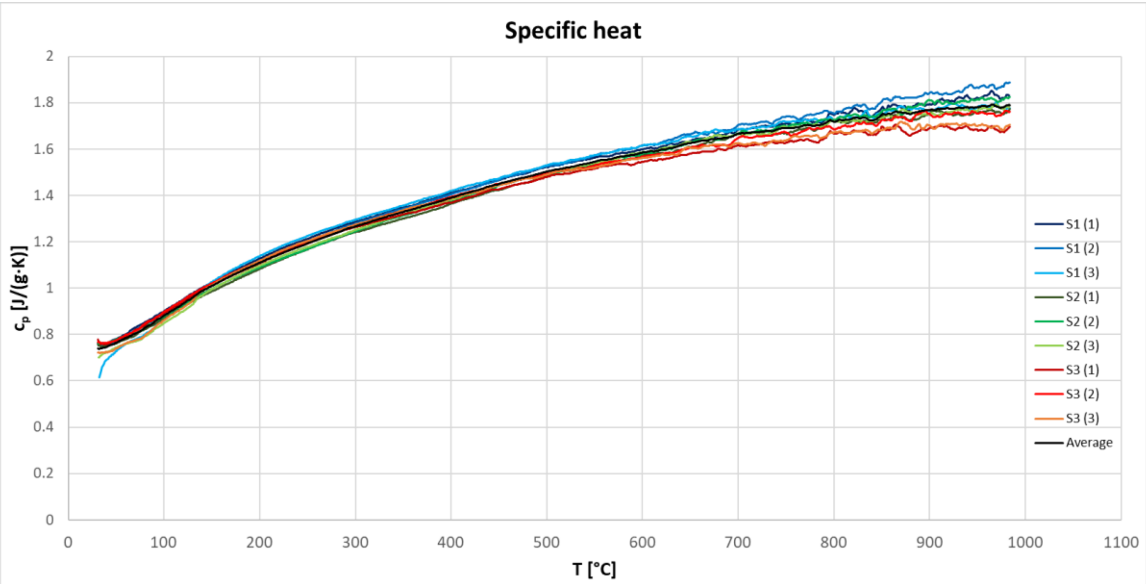

Figure 2 – CrGr specific heat as a function of temperature.

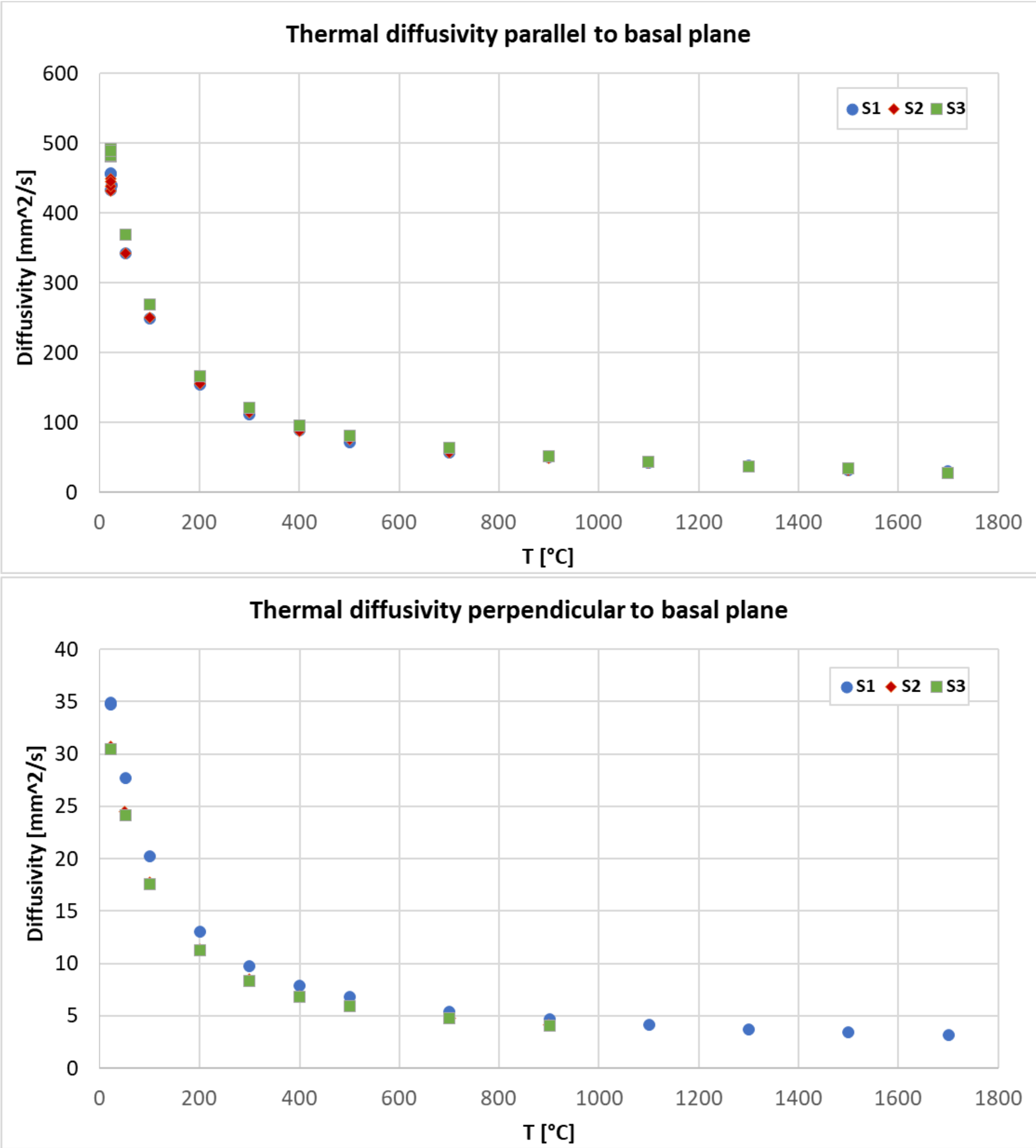

Figure 3 – CrGr thermal diffusivity parallel (top) and perpendicular (bottom) to the basal plane.

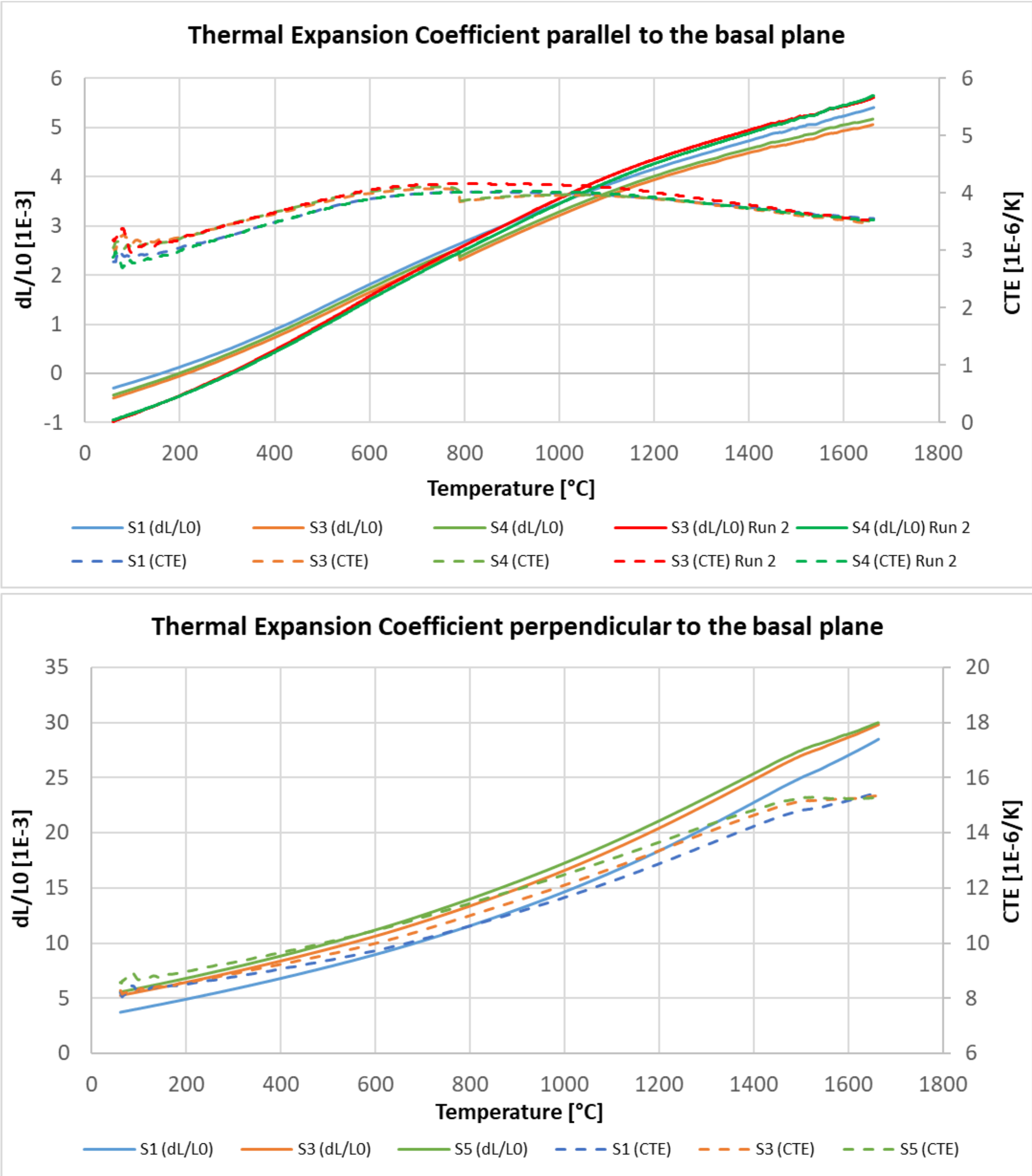

Figure 4 – CrGr thermal expansion coefficient parallel (top) and perpendicular (bottom) to the basal plane.

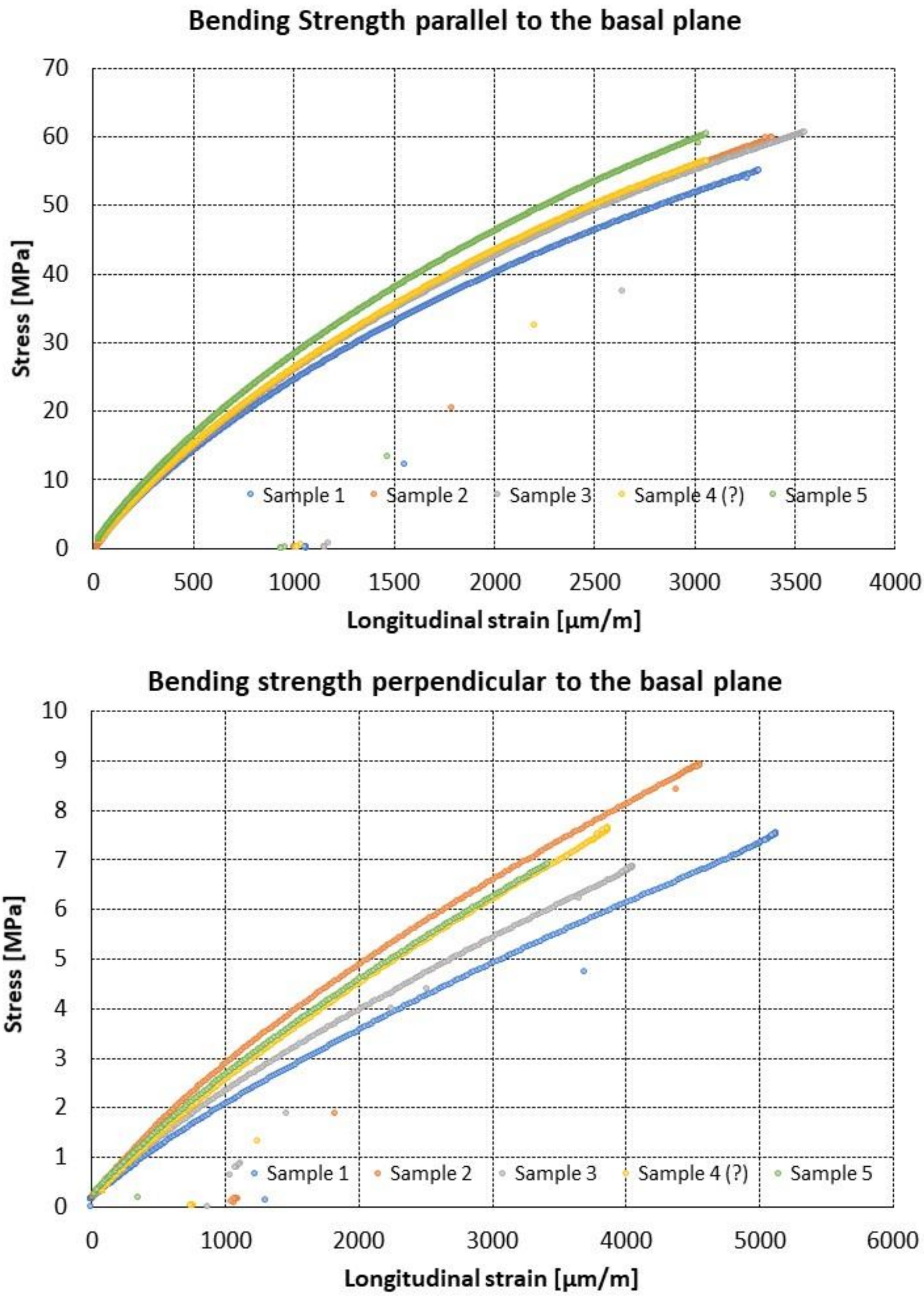

Figure 5 – CrGr bending strength parallel (top) and perpendicular (bottom) to the basal plane.

A summary of the results, compared to the technical specification, is given in Table 5. In red, we highlight the values which do not fit yet with the requirements.

Table 5. CrGr properties compared to the technical specification

	Specification		**CrGr Plate #1**		
Property	∥*	⊥	∥*	⊥	**Unit**
Density at 20ºC	2.40 – 2.60		2.32		[g/cm³]
Specific heat at 20ºC	> 0.6		0.687		[J/(g·K)]
Electrical conductivity at 20ºC	> 0.75		1.02		[MS/m]
Thermal Diffusivity 20ºC / 300ºC	> 350/100	> 20/6	470/120	33/9	[mm^2/s]
Thermal conductivity at 20ºC / 300ºC	> 500/280	> 35/20	750/350	52/27	[W/(m·K)]
Volumetric CTE 20-1000ºC	< 7		6.7		[$10^{-6}K^{-1}$]
Coefficient of thermal expansion 20-1000ºC	< 2.9	< 15	4.0	12.0	[$10^{-6}K^{-1}$]
Young's Modulus at 20ºC	35 < E < 75	5 < E < 8	46	3	[GPa]
Flexural strength at 20ºC	> 60	> 10	58	8	[MPa]
Flexural strain to rupture at 20ºC	> 2500	> 4000	3280	4200	[µm/m]
Dimensional stability	< 0.05	< 0.25	-0.05	0.45	%

With respect to the values not meeting yet the technical specification, one can observe that a density lower than 2.4 g/cm^3 is not necessarily a malus, since it implies a lighter material, which is in general desirable for common applications. In beam-intercepting devices, a minimum density is required for beam absorption, but the comparison in this sense are materials such as carbon-fibre carbon composites and isostatic graphite, used or proposed for use for example in the LHC collimation system. Such materials have a density of, respectively, 1.67 and 1.85 g/cm^3, so a density in the order of 2.3 g/cm^3 can certainly be acceptable. However, it should be excluded that the density lower than expected is not a symptom of a poor material compaction. This could be done via vacuum tests, foreseen at a next stage of the project.

For what concerns the mechanical strength, although the value in the two directions is still slightly lower than the specification, a significant improvement (factor of 5-6) has been observed with respect the starting point of the project, where the baseline for CrGr was in the order of 10 MPa in the best direction.

The dimensional stability of the material is still not excellent, meaning that the samples are still in a state of internal stress induced by the production cycle and not completely removed by a subsequent 3h annealing cycle at 1700 °C. This result can easily be improved via optimization of the post-sintering annealing cycle.

The overall summary of the results clearly show that CrGr, although still requiring some tuning and optimization in the next years of the project, is a very promising and important alternative to MoGr, with the significant advantage of a lower sintering temperature and, thus, an expected lower production cost.

5 Conclusions

The first year of work within IFAST WP4.4 led to important advancements towards the final objective of increasing the efficiency and reducing the cost of production of CCM. In particular, the production of CrGr at Nanoker demonstrated that a cheaper alternative to MoGr exists and must be pursued in the next years of the project.

The material, however, is not entirely matching the specified requirements yet. The proposed working plan for CrGr is thus:

1. Focusing on the Ø170 mm plate dimension, fine-tune the production parameters (composition, pressure, temperature, dwell time) to meet the specification. One possible example could be an increase of the metal content.
2. Upscale the production to 2x Ø170 mm plates per machine cycle, and verify the thermophysical properties.
3. Upscale the production to 1x Ø230 mm plate per machine cycle, and verify the thermophysical properties.
4. Upscale the production to 2x Ø230 mm plates per machine cycle, and verify the thermophysical properties.

In parallel, on the material already produced and on the next ones, we will also perform UHV tests, which are important for applications in HEP. Nanoker will also finely machine one of the plates to the shape of an HL-LHC secondary collimator absorber [5], and CERN will perform metrology measures to confirm machinability and evaluate phenomena such as material relaxation with time, which had been observed in some grades of MoGr.

The work performed in task WP4.4 is also relevant for other IFAST tasks, such as WP4.3, which investigates materials for beam windows. In fact, CCM are excellent candidates for such devices, which must withstand high-brilliance beams without experiencing thermomechanical damage. The WP4.4 team has produced samples for testing under ion irradiation in the scope of WP4.3 [6].

6 References

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Annex: Glossary

Acronym	Definition
CCM	Carbide-Carbon Materials
MoGr	Molybdenum-Graphite
CrGr	Chromium-Graphite
BID	Beam-Intercepting Device
SPS	Spark-Plasma Sintering