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Evaluation of Carbon/Carbon Composites for control rods –

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Evaluation of Carbon/Carbon Composites for control rods Deliverable 2.5

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Résumé

This report synthesizes the results of CEA-Grenoble HTR-M WP2 task on carbon-carbon (C/C) composites. This work aimed at evaluating the industrial grades of C/C for an application as a cladding material of HTR control rods on the basis of technical specifications given by Framatome.

This report firstly reviews the mechanical performances of available commercial grades and then compares the proposals of companies for the procurement of C/C tubes. Finally some recommendations will be drawn for the selection of the C/C material.

Screening tests of some candidate materials appear to be the next step to progress in the evaluation. Collaborations with manufacturers may be fruitful and seem possible to select or develop and qualify the grades.

Mots clés

HTR - Control Rods – C/C - composites

TABLE

I. Introduction

This report synthesizes the results of CEA-Grenoble HTR-M WP2 task on carbon-carbon (C/C) composites. This work aimed at evaluating the industrial grades of C/C for an application as a cladding material of HTR control rods on the basis of technical specifications given by Framatome [1].

Mechanical testing of composite materials, initially planned within the HTRM project, has been re-oriented in order to focus the task on collecting material data from suppliers and technical information from previous HTR research programs. CEA was in charge of managing technical discussions with different E.U companies: SNECMA, SGL and lately EADS-ST and also in charge of exploiting the past experience of FZ-Juelich center on C/C mechanical testing.

This report firstly reviews the mechanical performances of available commercial grades and then compares the proposals of companies for the fabrication of C/C tubes. Finally some recommendations will be drawn for the selection of the C/C material.

II. Performances of commercial grades

II.1 Influence of fabrication parameters

It is well established that many fabrication parameters have a strong influence on the mechanical performances of C/C structures. We can mention the following process parameters:

- Fiber and yarn properties: High Modulus fibers (400-600 GPa) have low values of rupture elongation (1%) though High Resistance fiber with lower stiffness (200-250 GPa) can reach higher elongation. Some grades developed by Snecma and Dunlop combine ex-PAN and ex-pitch fibers in their reinforcement. PAN fibers are used because of their higher modulus and thermal conductivity so that the composite properties can be tailored in a given direction. The fiber content per yarn sharply influences the mechanical strength. Japanese program reports that the tensile strength is higher with low count of fiber per yarn [2].

- Fibers matrix bonding: fibers surface morphology that can be adjusted by chemical deposition or controlled oxidation affects the adherence and shear strength of fiber/matrix interface. Specific fibers treatments are performed during fabrication in order to compensate the bonding degradation brought by the high temperature graphitization process [3].

- The distribution of residual porosity acts as initiation sites for delamination and affects the shear strength resistance of the composite. This characteristic depends on matrix densification process. For instance, Chemical Vapor Infiltration is less efficient to eliminate intra-yarn pores than the impregnation method based on capillarity, but more reliable to fill inter-yarn porosity. Both techniques could be combined to improve the mechanical performances[4].

- The architecture of the network of yarns (fabrics) is a design parameter for adjusting the performance of composite structure according to its mechanical loading. For 2D woven composites, fabrics could be stacked in preferential orientation or alternatively layered in order to give a more or less isotropic behavior. Fiber architecture in tubes could be adjusted in order to enhance either axial or tangential reinforcement. For plane 2D composites, needling is currently performed to improve properties through the thickness.

- Post densification heat treatments, such as graphitization, can be performed up to 2800°-3000°C. The graphitic structure is known to improve mechanical performances and dimensional stability under irradiation of C/C composites densified by resin impregnation [3].

The conditions of elaboration of industrial grades are a matter of fabricants and are often poorly described in the technical documentation where a commercial name can sometimes designate a family of materials obtained with slightly different process parameters. In this context, comparisons between grades are hazardous and technical discussions with suppliers are required to evaluate existing materials.

II.2 Thermo-mechanical properties

We have collected data related to the characteristics and performances of industrial grades issued from different programs listed in table 1. Fabrication parameters are summarized in the table 2.

Programs	C/C grades investigated
European research on fusion technology [5]	N11, N112, NS31, NB31 (Snecma) A05 (Le Carbone Lorraine) Concept 1-2 (Dunlop) CX-2002 U (Toyo Tanso)
German HTR project [6,7]	CC 1501, CC 1501 G, CC 2001 G (SGL)
Japanese HTTR project [2,8]	CX 270, CX 270 G (Toyo Tanso)
Other (mechanical testing) [9,10]	CF 222 (Shunk)

Table 1 : sources of data related to the mechanical performances of C/C grades

II.2.1 Mechanical strength

Figure 1 gives a comparison of some mechanical strength compiled from different sources (technical documentation, articles). It has to be noticed that information on the testing conditions (standard, sample orientation and geometry…) are often incomplete so only general trends can be drawn. It can be noticed that the mechanical resistance of the composite is linked with the constitutive fibers: basically, stiffer pitch fibers induce a higher Young modulus. Variability is important for PAN based composites but may be related to fiber grades, heat treatments or matrix properties. Higher mechanical properties of the Japanese CX 270 G grade seem to be correlated to the higher density of fibers (50 % vs 30-35 % for other C/C) and to the optimization in the fiber count per yarn. The scattering in the properties of SGL materials CC 1501 and 2001 could also be partly explained by the difference of fiber density considered in the tensile direction. Thus, orthotropic architecture of fiber leads to a stronger reinforcement in the 0° compared to the isotropic case where the density of fiber is lower in this direction. Finally, all felt-based C/C (short fibers) display lower values of mechanical strength.

The InterLaminar Shear Strength (ILSS) characterizes the sensibility of 2D composites to the damage by delamination. Values of ILSS of needled and non-needled 2D composites are reported on the figure 2. All commercial grades display low values of shear strength that constitutes a weakness of this material. Needling operations slightly enhances the resistance to délamination from 5-10 MPa to 15-20 MPa.

The mechanical properties of C/C are remarkably stable with temperature up to 2000 °C [11] as it is shown by the data reported on the figure 3. A trend towards a slight enhancement in the mechanical strength of all grades is even observed. It is currently explained by the decrease of the internal stresses with the elevation of the temperature.

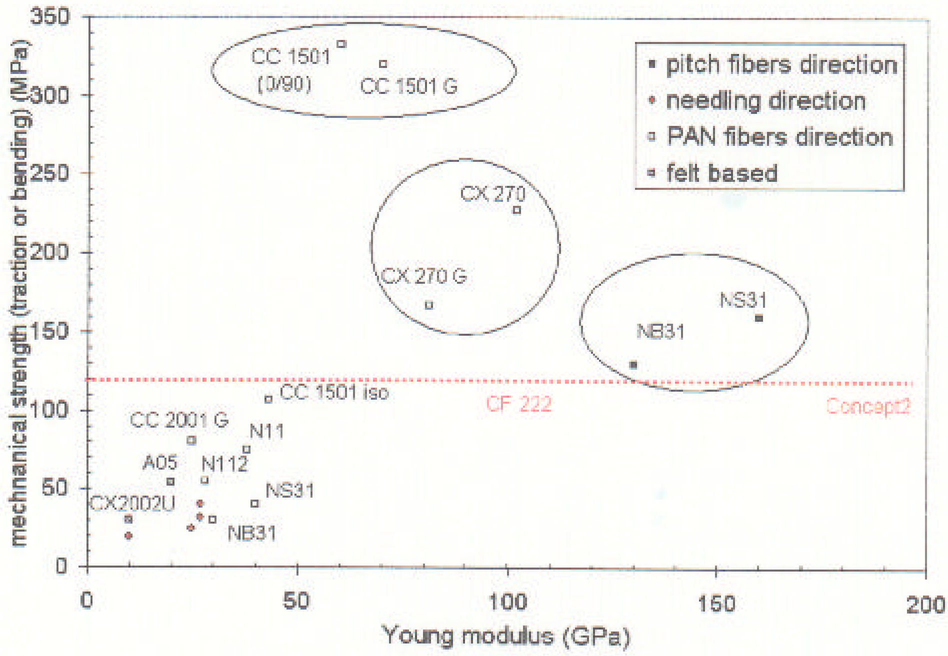

Figure 1 : Mechanical performances of 2D C/C at room temperature.

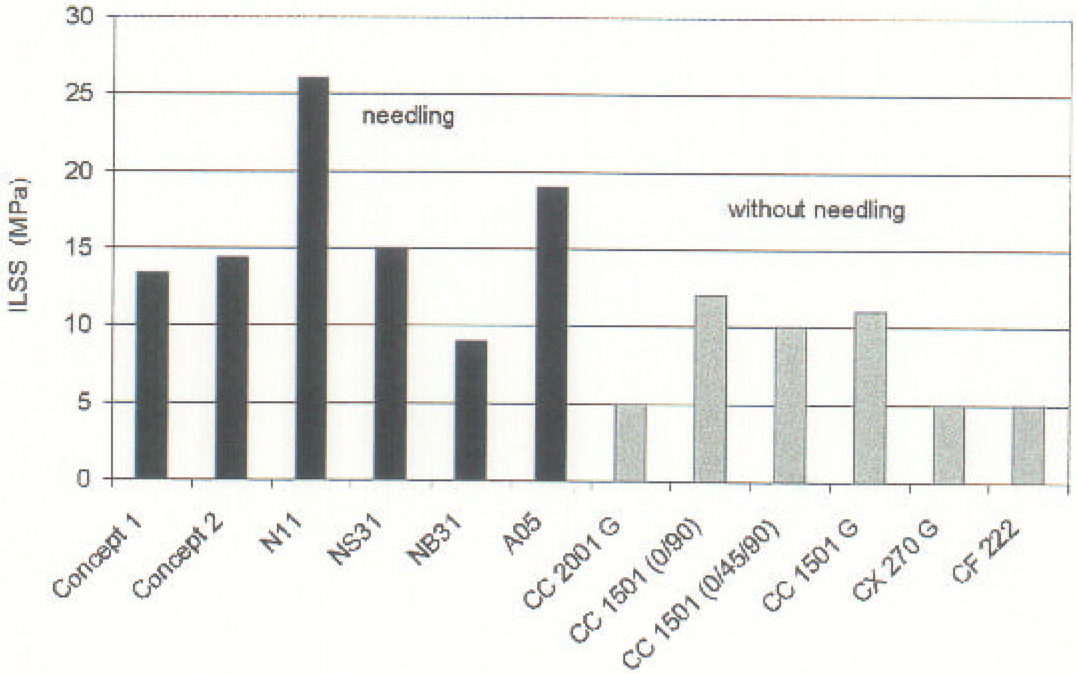

Figure 2 : InterLaminar Shear Strength (ILSS) of 2D C/C at room temperature.

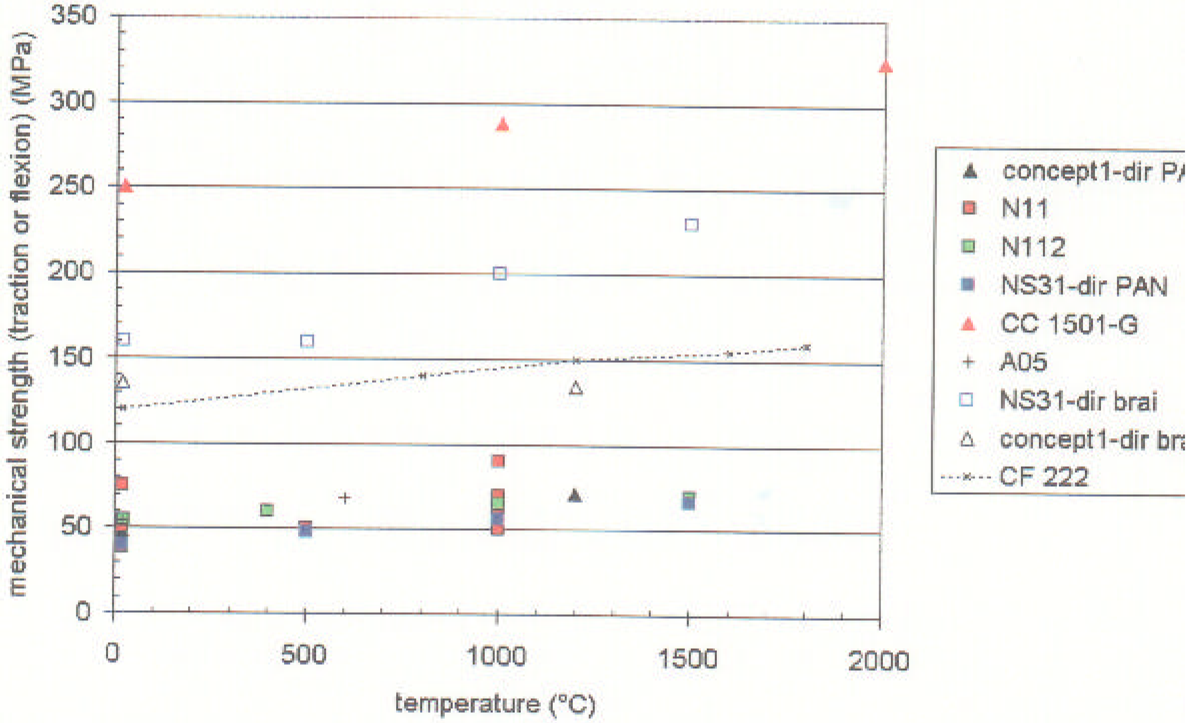

Figure 3 : Evolution of the mechanical strength of 2D C/C with the temperature.

II.2.2 Thermal conductivity

Thermal conductivity of C/C is related to the level of cristallinity of the matrix and fibers material. Room temperature values are scattered within the range of 5 – 500 $W.m^{-1}.K^{-1}$. Figure 4 shows the evolution of this property with temperature. The differences between grades are lower at 1000 °C since the thermal conductivity decreases sharply for grades having higher conductivity at R.T.

For Concept-1 and NS31 products, the use of pitch fiber allows improving the thermal conductivity by a factor 2-3 in the direction of fibers. The temperature of graphitization also plays an important role. The values of thermal conductivity at R.T typically rise from 20 to 180 $W.m^{-1}.K^{-1}$ after a treatment at 2800 °C [11]. The temperature of graphitisation of SGL CC 1501 material (2000 °C) explains its lower thermal conductivity.

II.2.3 Thermal shock resistance

Thermal Shock Resistance (TSR) of materials is currently evaluated from the following relation:

$$R_{th} = \frac{\sigma_r \lambda}{E\alpha} \qquad (1)$$

where σr is the strength, λ the thermal conductivity, E the Young modulus and α the constant of thermal expansion.

Deng [11] has characterized the thermal shock resistance of felt-based 2D C/C composites in a wide range of temperature. These results, plotted on the figure 5, show that the TSR increases sharply after a graphitization at 2800°C. At room temperature, the values are 10 times higher than the values obtained on the same material without graphitization. Within the range of 1500 and 2000°C, values are 2-3 times higher. The main contribution to the TSR is brought by the thermal conductivity that is greatly enhanced by graphitization.

Values of TSR of commercial grades are also plotted on the figure. Due to the lack of data, few values could be calculated from the basic properties. We have also distinguished, when possible, the different directions of the composite.

Grade N11 elaborated with PAN fibers has a higher TSR résistance (160 $kW.m^{-1}$ at 1000°C) thanks to a high temperature treatment of graphitisation. For the anisotropical NS31 grade (graphitized at lower temperature), TSR is higher in the pitch-fibers direction (410 $kW.m^{-1}$ at 1000°C) than the value in the direction of PAN-fibers (40-50 $kW.m^{-1}$).

Finally, in the needling direction, values of TSR range from 20 to 50 $kW.m^{-1}$ at 1000°C.

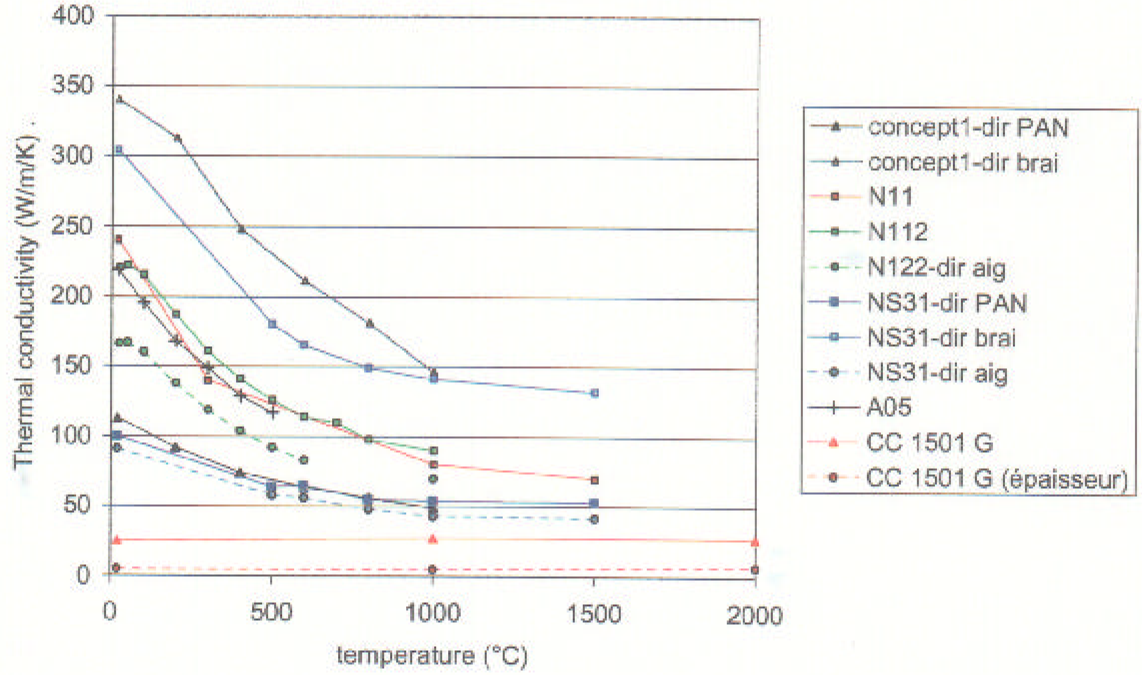

Figure 4 : Evolution of thermal conductivity with the temperature for different 2D C/C.

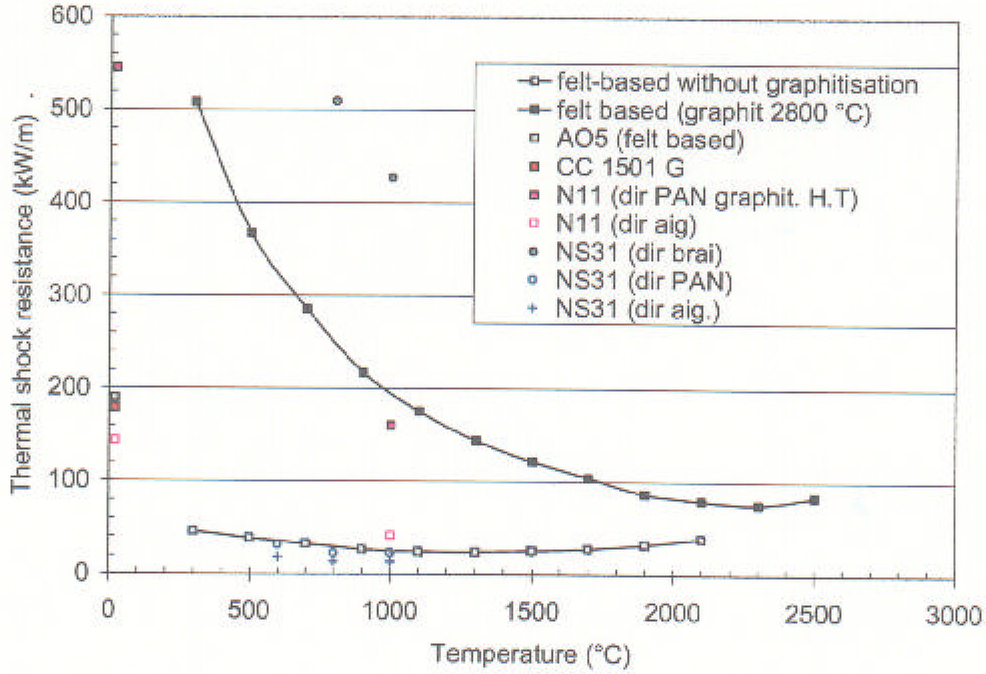

Figure 5: Evolution thermal shock resistance with the temperature for different 2D C/C.

Commercial name	Supplier	Fiber architecture	Ma-trix	Post densification treatments	Densi Poros
Concept 1	DUNLOP	2D weaving of ex-pitch fibers (P120-130) + needling of PAN fibers. Fibres content 30 %			1,87/6,
Concept 2	DUNLOP	2D weaving of ex-pitch fibers (P120-130) + needling of PAN fibers. Fibers content 38 %			1,85/6,
DMS 678	DUNLOP	2D weaving of ex-PAN fibers	CVI		1,72
SEPCARB N1	SNECMA	PANOX fibers + needling. Fibers content 27 %	CVI	Graphitization 2500 °C	1,75/10 %
SEPCARB N11	SNECMA	NOVOLTEX Texture (2D + needling of ex-PAN fibers) Fibers content 30 %	CVI		1,8/10
SEPCARB inox NS31	SNECMA	2D weaving of ex-pitch P55 (80%) et ex PAN fibers (20%)	CVI	Impregnation SiC (8-10 %)	2,05/3- %
SEPCARBN S11	SNECMA	NOVOLTEX Texture (2D + needling of ex-PAN fibers)	CVI	Graphitization 2200 °C + Impregnation SiC	2,13 / 1
SEPCARBN B31	SNECMA	2D weaving of ex-pitch P55 (80%) and ex PAN fibers (20%)+ needling. Fibers content 35 %	CVI	Final impregnation with pitch resin	1,9 / 8
SEPCARBN 312B	SNECMA	NOVOLTEX texture (2D) of ex-pitch P25 (80%) and ex-PAN (20 %) fibers + needling	CVI	Graphitisation 2800 °C + pitch impregnation 1000°C/1000 bar	
SEPCARBN 112	SNECMA	NOVOLTEX texture (2D) of ex-PAN fibers + needling. Fibers content 30 %	CVI	Graphitisation 2200 °C + pitch imprgnation	1,95 / 6
Aerolor A05	Carbone Lorraine	Felt of ex PAN fibers + needling Fibers content 25 %	CVI	Graphitisation > 2500 °C + pitch impregnation	1,95 / 7 %
CC 2001G	SGL	Fibers winding	Imp	Graphitisation 2000 °C	
CC 1501	SGL	Orthotropic stack of 2D plies (0/90°) or quasi isotropic stack (0/+45/-45/90)	Imp		
CC 1501G	SGL	orthotropic stack of 2D plies (0/90°) or quasi isotropic stack (0/+45/-45/90)	Imp	Graphitisation 2000 °C	
CX-2002U	Toyo Tanso	2D Felt of ex-PAN fibers			1,64
CX 270	Toyo Tanso	2D weaving of ex PAN fibers	Imp		
CX 270 G	Toyo Tanso	2D weaving of ex PAN fibers Fibres content 50 %-	Imp	Graphitisation 2800 °C	1,69
CF 222	SCHUNK	2D weaving satin 8H (0/90°)			

<u>Table 2</u>: Fabrication characteristics of commercial C/C grades (CVI : Chemical Vapor Deposition, Imp : Impregnation).

II.3 Past experience of FZ-Juelich on the characterization of SGL grades

In the 80's, C/C composites were studied at the Juelich research center in the frame of the German program on HTR [12]. C/C tubes were tested in order to evaluate the capacity of this structure to constitute some parts of the Hot Gas Duct. CEA Grenoble has contacted the members of the research team in order to collect their experience [13]. M. Roedig tested tubes from SGL (CC 2001 G) under internal pressurization and compared the results with the values obtained with the split-disk test. A specific care was brought in order to avoid stress concentration at this end of tubes exerted by the sealing system [14]. This experience constitutes a valuable guideline for performing mechanical testing on composite tubes.

The results reported on the figure 6 show that industrial tubes (325 mm diameter and 4 mm thickness) with a fiber reinforcement designed for diametrical loading can sustain a tangential stress up to 400 MPa.

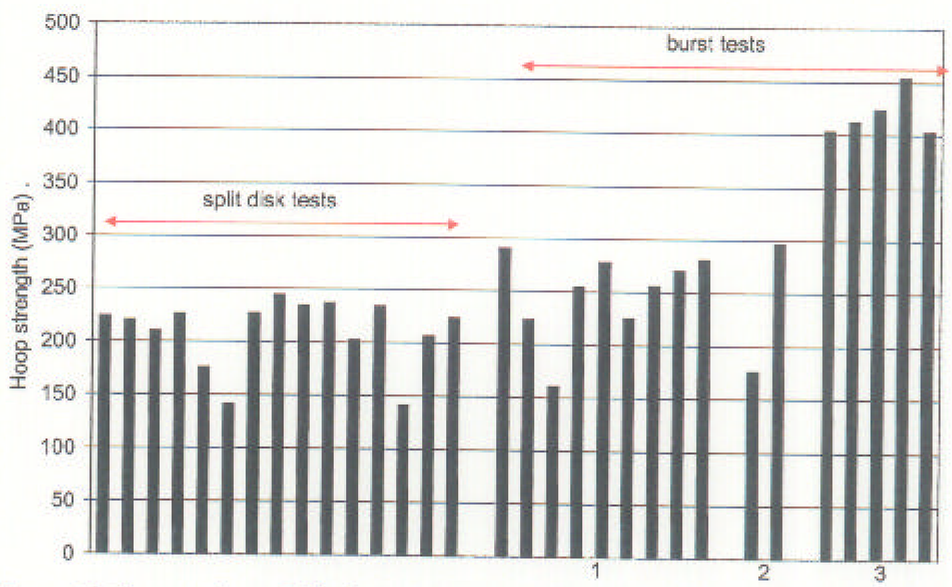

Figure 6: Comparison of the hoop stress at rupture determined on C/C tubes by split-disk tests and burst tests He (1) water (2) and (3) after optimization of the test.

III. Evaluation of E.U suppliers of C/C composites

CEA Grenoble has early contacted SGL and SNECMA for the procurement of C/C components (tubes and molts) in order to perform mechanical testing, as initially planned in the project. A maximal operating temperature of 1600 °C and a mechanical resistance of 30 MPa in tension (10 MPa for shear stress) were specified. Both companies provided commercial proposals that have been previously analyzed [15]. Without regarding irradiation or environment effects, it was stated that current commercial grades N11 (Snecma) Sigrabond 2001 G (SGL) could satisfy the requirements.

Technical discussions with manufacturers have been pursued in 2004. Framatome and CEA have jointly conducted the evaluation of manufacturers (SGL and EADS). Information collected during visits and meetings are summarized below.

III.1 Snecma

III.1.1 Background

The initial proposal of Snecma consisted in the procurement of tubes of SEPCARB N11 for mechanical testing. This C/C is a 3D composite reinforced with PAN fibers woven and needled. PyC matrix is densified by CVI operation eventually followed by a high graphitization step at high temperature and additional densification.

III.1.2 Perspectives

We have just analyzed the commercial proposal from Snecma. We have completed our evaluation with published data on N11 that is rather well known since it has been widely studied in the European fusion program. For plane geometry, the typical tensile strength is about 50 MPa, the compressive resistance is close to 100 MPa though the shear strength is about 20 MPa. As previously stated, Snecma proposed a costly solution due to the fact that their capability of production greatly exceed our demand.

No further technical contacts occurred in 2004 with Snecma in the frame of the HTR-M program. Indeed, it has appeared that such discussions should be undertaken in the frame of a confidentiality agreement because of the sensitivity of material data.

III.2 SGL Technologies

III.2.1 Background

The main activity of SGL consists in the production of graphite components for industry (electrodes for metallurgy, heating or intern for ovens, tooling, ...). C/C composites are manufactured in Meitingen and in California and represent about 25% of the company's cash flow. SGL also manufactures PAN based fibers in Scotland for brake disks but currently purchases commercial PAN fibers from Japan or USA. The company is equipped for performing all the composites built-up operations: weaving or winding of rovings, impregnation of prepregs (resin) and matrix densification. Densification can be achieved by impregnation of phenolic or pitch resin or liquid impregnation of SiC. As a consequence, several process parameters can be adjusted for a given application (kind of resin, additives...) The factory of Meitingen is going to implant equipments for performing densification by Chemical Vapor Infiltration.

SGL could supply different grades of C/C. Tubes, plates and shaped pieces, bolts can be purchased according to specifications listed in the SGL's commercial catalogue. For special applications, the recently created R&D Department of Meitingen could develop specific materials. Mechanical testing, compression and bending up to 2500°C, could also be performed in Meitingen.

III.2.2 Perspectives

During the visit, SGL seemed to be opened to develop a global design of the control rod system, including the definition of the unit segment, the articulation between segments and the guidance device of the rod. Mechanical performances of current grades appeared to be acceptable regardless of the environment effects (irradiation, oxidation). Moreover, SGL seem ready to adjust several process parameters (fibers, architecture of reinforcement...) in order to develop an optimized grade for use in severe environments, as far as data on irradiation effects are available.

III.3 EADS-ST

III.3.1 Background

EADS-ST sites are implanted in France and in Germany (Ottobrunn). Opposite to SGL or SNECMA, EADS-ST doesn't supply commercial grades of C/C but is rather specialized in the built-up of multidirectional performs (2D, 3D) by weaving.

Massive 3D perform can be elaborated by tri-orthogonal weaving but also "polar" reinforcement (in the radial direction) can be performed in order to obtain tubes with an actual 3D fiber structure. EADS could also subcontract specific operations of densification.

III.3.2 Perspectives

EADS-ST seems to have a strong experience in the design of composites structures and a competence in the definition of constitutive material (fibers, matrix, depositions) according to given specifications (mechanical, environment). EADS proposals could also include industrialization of the fabrication process and mechanical characterization of materials.

IV. Conclusion and recommendations

The evaluation and comparison of the mechanical performances of commercial grades from technical papers are not straightforward because both process parameters (that is matter of manufacturers) and testing conditions are poorly described. In spite of this lack of data, it appears that mechanical properties and thermal conductivity could be easily fitted by material suppliers in order to reach the specifications, regardless irradiation or environment effects.

Otherwise, technical discussions have shown that all manufacturers need information about the behavior of constitutive materials under irradiation. More particularly, the dimensional evolution of C/C under neutron flux seems to be important for the selection of an existing grade or the design of a new material. If the trend toward a better stability of pitch based material is stated (due to their graphitic structure), the use of this kind of fibers will have to be specified. Other environmental effects should also be taken into account, especially the corrosion risks that could occur due to air ingress during accidental situations. Protective depositions or matrix additives could be proposed by manufacturers to limit the material oxidation.

Screening tests of some candidate materials appear to be the next step to progress in the evaluation. Collaborations with manufacturers may be fruitful and seem possible to select or develop and qualify the grades.

V. References

[1] B. Riou, HTR-M Design use and specification for internals, HTR-M-01/7-D2.1.14.

[2] T. Sogeti, M. Ishihara, S. Baba, T. Kojma, Y. Tachibana, T. Iyoku, T. Hoshiya, T. Hiraoka, M Yamachi,. JAERI Research Report 2002-26.

[3] Chung D.D.L. Carbon fiber composites, Butterworth-Heinemann ed.(1994).

[4] F. Gao, J.W. Patrick and A. Walker, towards the optimisation of the densification of PAN-based carbon-fibre-reinforced carbon laminates. Composites Science and Technology.

[5] J.P Bonal, C.H. Wu, Neutron irradiation effects on carbon based materials at 350 °C and 800 °C, Journal of Nuclear Material 277 (2000) 351-359.

[6] G. Popp, U. Gruber, H. Böder, K. Jansen, Graphite and Carbon/Carbon components for hot gas duct, IAEA Specialists' Meeting on Heat Exchanging components of Gas-Cooled Reactors, Düsseldorf 16-19 April 1984.

[7] Documentation SGL – SIGRABOND.

[8] S. Ishiyama, K. Fukaya, M. Eto, Strength test of C/C composite high performance control rod for FTGR. Journal of the Atomic Energy Society of Japan. Oct. 1999; 41(10).

[9] B. Thielicke, Mechanical properties of C/C composites, Key Engineering Materials vol 164-165 (1999) pp 145-150.

[10] U. Soltész, R. Schäfer, B. Thielicke, Determination of the interlaminar tensile strength of a C/C by the diametrical compression test at temperature up to 1800 °C. Key Engineering Materials vol 164-165 (1999) pp 167-170.

[11] J. Deng, W. Liu, H. Du, Thermal shock resistance of C/C composites, Carbon vol. 37 (1999) 1868-1869.

[12] M. Roedig, W. Baur, B. Woschek, Burst tests to measure the tangential strength of CFC tubes. AIEA (1991).

[13] G. Delette, Past experience of FZJ on C/C mechanical testing for HTR Reactor development – Report on meeting and discussions with FZJ experts. N.T DTEN/S3ME/LA2M/2004-006.

[14] B. Woschek, M. Rödig,. Report FZJ IRW-TN-40/91.

[15] G. Delette, R. Couturier, HTRM Project Carbon/Carbon composites for control rods: reports on discussion with manufacturers. R.T DTEN/DL/2004-017.