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Synthesis of preferred C/C Composite Materials for the VHTR Control Rod

Author(s): **Isabelle Hugon (CEA)**

Contributor(s) **K Hingst (SGL)**
O Gelineau (AREVA-F)
B-C Friedrich (AREVA-G)
J. Hegeman (NRG)
M. Davies (NNC)

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Document title

Synthesis of preferred C/C Composite Materials for the VHTR Control Rod

Abstract

A technical synthesis of potential Carbon Composite materials for the VHTR Control Rod and other components has been performed and recommendations made concerning selection and testing. Potential materials include 2D materials using filament winding (for cylindrical shapes) and pressing for the connecting parts with enhancements (e.g. SiC coating) for protection against oxidation. Material testing should ideally be carried out on both small and large sized samples (flat and round) taking account of available information on standards and experience. A draft test programme has been outlined focusing on effects of irradiation and oxidation and making use of available test facilities within EXTREMAT.

Revisions

Rev.	Date	Short description	Author	WP Leader	SP Leader	Coordinator
00	dd/mm/yyyy	First issue	Name, Organisation	Name, Organisation *Signature*	Name, Organisation *Signature*	Name, Organisation *Signature*
01	31/10/2006	First issue	Isabelle Hugon CEA	Isabelle Hugon CEA	Derek Buckthorpe NNC	

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1 Introduction & Scope

Carbon Fibre Composites (CFC's) are identified as potential materials for several structural parts of the VHTR (Very High Temperature Reactor, T°>1000°C, Helium gas cooling) due to the high operating temperature of the reactor. The main structural components that could be manufactured with CFC are control rods and some other components like pipes, straps or supports.

This document (DML2.1), which is part of RAPHAEL-IP/SP-Materials/WP2 (high temperature materials), deals with the potential use of carbon/carbon (C/C) composite materials in VHTR and consists of:

- a review of technical specifications for control rods or other applications,
- a description of recommended C/C composite materials for such applications.
- some recommendations on material testing
- a list of key issues to prepare future test programme.

2 Specifications for control rod & other applications

These specifications are based on past information defined within the HTR-M and EXTREMAT projects [1, 2] with some additional information available for such applications.

2.1 <u>Control rods</u>

2.1.1 Description of material application

- The materials envisaged for control rods must support boron carbide compacts. Two systems are considered :
    - o Control rods located in the side replaceable reflectors at the boundary of the core ensuring the reactivity compensation and emergency protection. They are inserted to varying heights for control during operation and completely inserted for protection.
    - o Automatic control rods used only during start up/shutdown and refueling operation, located in the active core at the boundary with the inner reflectors. They are completely removed when the core is critical.

Control rods consist of several segments connected to each other, containing the absorber material. Each control rod assembly is supported by mechanisms in the top head of the reactor.

2.1.2 Environmental conditions

Assuming here that a part of control rods is devoted to start-up/shutdown and another to reactivity control + shutdown, this means that the former will be less solicited in normal operation (withdrawn when reactor critical) than the latter. Nevertheless, in accidental conditions, same conditions must be withstood by both types of control rods. The following table gives the environmental conditions:

Table 1 Environmental Conditions for Control Rods

	Start-up/shutdown control rods	**Operating control rods**
Nominal conditions		
• Temperature	T = 400°C	400°C < T < 1100°C
• Medium	He with small quantity of : H_2O (1 to 5ppm H_2 (200ppm) CO (50ppm)	He with small quantity of : H_2O (1 to 5ppm) H_2 (200ppm) CO (50ppm)
Pressure	50-70 bars	50-70 bars
Air ingress accidental conditions (without irradiation)		
• Temperature	1200 < T < 1400°C during 100 h 1400 < T < 1500°C during 150 h	
• Medium	air	
Max. n fluence (dpa)	~0	4
Expected life duration	30 years	30 years

2.1.3 Composition

The impurity level has to be controlled to limit the radioactivity of the material after irradiation (to minimize waste management) and to prevent from excessive oxidation. The highest purity level will have to be chosen for HTR applications.

Table 2 Suggested Allowable Impurity Levels

Element	Effect	Allowable level: value < (ppm)
Cl	Radioelement generator	5
N		50 (the quantity of N needs to be reduced as much as possible)
Co		0.1
Ni		1
Li		0.1
U		0.005
V	Oxidation catalyst	2
Ti		2
Fe		2
Ni		1
Pb		0.1
Cr		0.5
Cu		0.5
B	Neutron absorbent	Not limited
Li		
Cd		
Sm		
Eu		
Gd		
Dy		
Hf		

The maximum amount of ashes shall be less than 100ppm.

It is important to note that the values given for oxidation catalyst are preliminary values that will need to be refined because of the catalyst and inhibitive combination effects.

2.1.4 Product characteristic

Control rods consist of several segments connected to each other, containing the absorber material. Each control rod assembly is supported by mechanisms in the top head of reactor.

Existing control rods are made up of 2 concentric tubes with absorber materials in between. The outer tube diameter is about 100/120 mm and the inner tube diameter is about 60/70 mm. Their thickness is between 4 and 8 mm. The length of one segment is between 400 and 800 mm. A space inside the rods shall be let to the cooling of the rods.
A flexible structure shall connect 2 segments to each other. The total length of the rod is about 9 m.
Regarding the fabrication of these structures, the properties should not vary in large proportions between lots which mean that the fabrication process shall be reproducible. The following picture shows the design of the GT-MHR control rods. For the moment, no design is available for VHTR control rods.

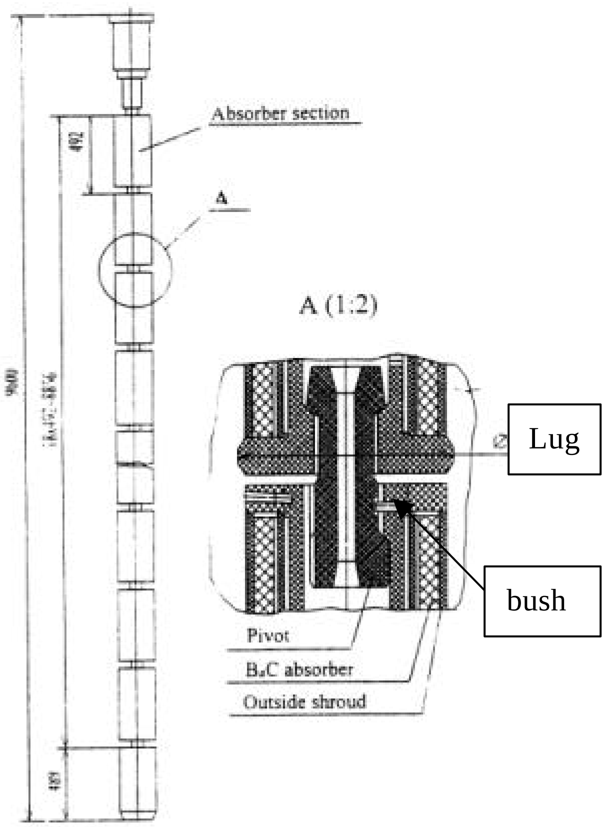


Figure 2-1 Schematic of VHTR C/C/ Composite Control Rod

2.1.5 Electrical and mechanical properties

Table 3 Electrical and Mechanical Property Requirements

	Specified value at room T° without irradiation		Specified value at T°=400-1100°C and under irradiation (fluence 0-10^{22} n/cm²)	
Measurement direction	*Radial*	*Circumferential and axial*	*Radial*	*Circumferential and axial*
Thermal conductivity ($W.m^{-1}.°C^{-1}$)	n.s.	30<?<150	n.s.	>20-30
CTE (K/m)	n.s.	n.s.	n.s.	n.s.
Tensile mechanical strength (MPa)	n.s.	>70	n.s.	>70
Bending mechanical strength (MPa)	n.s.	>70	n.s.	>70
Compressive mechanical strength (MPa)	n.s.	>70	n.s.	>70
Interlaminar shear Stress (MPa)	n.s.	n.s.	n.s.	n.s.
Fracture toughness ($MPa.m^{1/2}$)	n.s.	>10	n.s.	>10
Elastic constants (E, G, ?)	n.s.	n.s.	n.s.	n.s.
Thermal shock resistance $\lambda R_m/(E\alpha)$ (W/m)	n.s.	>65000	n.s.	>65000
Wear resistance	n.s.	n.s.	n.s.	n.s.

n.s. = not specified for the moment

2.1.6 Stability

The criteria for Wear resistance has not been established yet.

No criteria is specified for the moment for creep resistance under impure helium (T°~1000°C, ~5MPa, 10-30 years)

Dimensional changes after irradiation: < 2% for each direction and after a dose of 4dpa.

Air reactivity: No criterion is available yet.

Compatibility with B_4C.

2.2 Other applications

Some other components like straps or pipes could be made with composite materials. They are not described in this document because they are less critical (lower temperature and/or less fluence) and we have less information on the technical requirements.

3 Description of recommended materials

Carbon composites have to be tailored for each application to meet design requirements. Indeed, there is no off the shelf product and the following manufacturing parameters have to be adjusted to fulfill the technical requirements:

- Fiber nature, fiber architecture, preform manufacturing process
- Matrix nature, densification process, thermal treatment, with or without anti-oxidation protection.

These parameters might be different for each part of the components (co-axial tubes, lids, connecting system …) which might induce the selection of different composites grades.

3.1 Potential materials

The potential materials suggested by SGL are 2D carbon composites materials.

These materials should be manufactured by filament winding for the tube shaped materials and by pressing technology for the connecting parts.

Suggested matrix systems: resin/pitch matrix and/or CVI matrix.

Fiber reinforcement:

- pitch and/or PAN based fibers for the tubes
- pitch and/or PAN based fibers for the connecting elements

Temperature treatment: up to temperatures of 2000°C, alternative more than 2700°C.

The finished parts will be purified (less than 20ppm) and SiC coated for improvement of the oxidation properties.

3.2 Manufacturing parameters

- Fibre type

- Pitch and/or PAN based carbon fibers for the tubes
- pitch and/or PAN based carbon fibers for the connecting elements,
- Fibre supplier : SGL
- Tow size (number of filaments per tow) : min of 3k materials

- Fiber preform

– 2D
– Manufacturing process of the CFC parts will be hand lay-up and weaving for the connecting elements, and filament winding for the tubes
– Fiber content and orientation has to be defined within the project

- Densification and carbonisation

– Use of prepreg (phenolic resin) for the connecting elements
– Type of densification : pitch (isotropic pitch, coal tar pitch or petroleum pitch), CVI and/or mixed of both
– In case of mixed densification (liquid pitch/resin impregnation and CVI), the number of densifications will be 3 to 10
– Carbonization temperature: app. 1000°C for liquid and mixed densification

- High temperature thermal treatment

– T°: carbonization at app. 1000°C
– Graphitization at app. 2200°C (alt. app 2700°C)

- Purification treatment

– at min temperature of 2000°C
– with purification gas flow

- Machining

– by using standard tools for graphite machining,
– if necessary the parts will be machined in a clean machining shop
– Surface roughness after machining has to be defined

- Manufacturing control

– Will be defined accordingly to SGL experience with graphite and CFC reactor grade materials.

3.3 Impurities level

The impurity level should be controlled by chemical element analysis of the material.

SGL composite materials will have less than 20ppm ash content.

3.4 Availability of supply

The availability of supply will have to be guaranteed for more than 15 years. Indeed, the same grade of raw materials (fiber type, pitch grade, a.s.o…) and the same manufacturing processes will have to be used during material qualification and final components manufacturing.

3.5 Material properties

Density: more than 1,4 g/cm³

Fibre rate: more than 50 percent by volume

Open Porosity: less than 20 %

The mechanical properties (tensile strength and Young modulus) at room temperature and in the temperature range 400-1500°C can't be specified for the moment because they depend on parts. Stress strain curves should be provided so as to check the material behavior.

Concerning the creep resistance (bending creep or tensile creep) under inert atmosphere and slightly oxidizing atmosphere (T~1000°C, ~5MPa, 10-30 years), the measuring method has to be defined.

In the same way, thermal properties (thermal diffusivity and specific heat or thermal conductivity) and specific electrical resistivity depend on parts and will be given later.

At last, oxidation resistance properties will have to be measured but the measuring method has to be defined because it depends strongly on the testing method.

3.6 Feasibility of cylindrical structures

The manufacturing of cylindrical structures such as control rods claddings is easy to perform by filament winding according to the specified geometry.

3.7 Cost evaluation

No cost evaluation can be made for the moment because it depends very strongly on the fiber lay-up and on the manufacturing methods.

4 Recommendation on material testing

This chapter contains recommendation on material testing of both small samples and large structure. These recommendations, based on past experiments of each partner, is divided into two parts:

- The choice of representative samples:
  - geometry effect issue (links between flat samples and tubes)
  - samples as representative as possible of the final material (in term of fiber content, fiber architecture and residual stresses)
  - size effect issue (links between small and full size samples)
- The testing procedure itself (use of standards, reproducibility between specimens from the same batch and from various batches, tubes testing, …).

4.1 Recommendation on the choice of representative samples

- Material testing should be performed on the following sample geometry:
  - flat samples for the connection elements
  - round samples for the tubes (samples cut out of hole thick tubes or rings)

- Advice on size effect issue:
  - The size of the "representative elementary volume" will define the minimum size of mechanical test specimen
  - Some properties can be extrapolated from small samples to large cylindrical structure
  - Some other properties have to be measured on representative components (large tubes sections)

4.2 Recommendation on the testing procedure

Standards, reproducibility, dispersion, anisotropy

Composite materials are inhomogeneous and most of the time anisotropic. Moreover, there is a lot of dispersion in the same batch and between batches. These points induce to perform a high number of tests in the qualification phase, particularly to estimate the mechanical properties in each fiber direction, the dispersion of these properties and the reproducibility between lots.

Some European standards exist for thermal and mechanical test of Ceramic Matrix Composites (CMC), included C/C. These standards recommend making 5 to 10 measurements to obtain confident results and 30 measurements to have a statistical approach. They are restricted to flat samples testing.

Concerning tensile tests, specific grips (hydraulic grips or self-clamping grips) have to be used for composite materials to avoid failure in the clamping zone. To be noticed that high temperature tensile tests have to be performed under inert atmosphere to avoid oxidation of the composite.

Specimen size has to be fitted to the fiber pattern ("grain size") of the material so as to be representative. This leads to rather large specimen compared to metallic specimen because of the coarseness of composites "grain size". This could be a problem for the measurement of mechanical properties on irradiated materials because specimen size is limited by the available space in irradiation capsule (in the experimental rig, the samples are mounted on sample holders put themselves in small capsules Φ~25mm, H~500mm).

Tubes testing

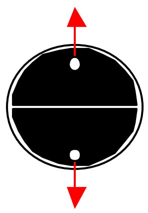
Concerning tests on tubular structures, there isn't any standards for CMC.

However, there are some European and American standards concerning Organic Matrix Composites tube tests. Two main tests are described in these standards: the split-disc test (ASTM D2290, NF EN 1394) and the burst test (ASTM D1599, NF EN 1394). The "split-disc test" consists in loading a ring through a self aligning split disk test fixture which applies tensile stress to the ring. The main drawback of this test is the bending moment that is induced during the test at the split between split disk test fixtures. The "burst test" is used to determine failure pressure of plastic pipes. Some other tests performed on strips cut out of tubes are also described in NF EN 1394.

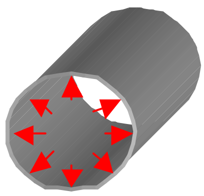
Despite the fact that these standards are dedicated to organic matrix composites, we can take inspiration from them to determine the circumferential tensile strength of CMC tubes.

The "internal pressurization test" (or "burst test" if the failure of the tube is reached) could be used to simulate the internal pressurization imposed by the absorbent in case of irradiation induced swelling for example. This test is particularly interesting to test large structure and to get true circumferential tensile strength (no bending moment). However, special attention should be paid to avoid stress concentration at the end of the tube during the burst test. This kind of test has already been used by FZJ in the 80's in the frame of German program on HTR. The results of the past experience of FZJ have been already described in HTR-M (WP2 deliverable 2.5[3]). They have pointed out that the hoop stress measured by burst test after optimization of the testing procedure was higher than that measured by split disk test, which confirm the negative effect of the bending moment in split disk test.

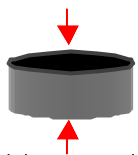
Some other test like axial compressive test could also be performed to determine the resistance of the control rods in case of accidental drop.



Diametric tensile test (Split-disk test)



"Internal pressurization test", "expansive mandrel test" or "burst test"



Axial compressive test

These tests should be performed on quasi full-scale tube, if possible. A correlation should be made with the results obtained on flat samples.

At last, full-scale component tests as representative as possible of the final structure will have to be performed.

Oxidation tests in the temperature range [400-1400°C]

The testing procedure has to be evaluated within the project

Non destructive tests of composite materials (tubular structures)

The testing procedure has to be evaluated within the project

5 Key issues & draft test program

5.1 Key issues

The main issues for the R&D program on composite materials for control rods are the followings:

- The irradiation effects at high temperature (4.3 10^{21} n/cm² within 30 years)
- The oxidation resistance at high T° (under impure He or in air in case of accidental air ingress)
- The design of the components

Irradiation effects

Control rods are submitted to rather high irradiation fluence which may induce many kinds of material damages like:

- Dimensional changes (due to the axial shrinking and the radial swelling of the carbon fibre itself),
- Drop of thermal conductivity,
- Mechanical properties changes, including potential irradiation induced creep.

On the point of view of the manufacturing parameters, the following trends seem to come out according to past irradiation results obtained on “fusion” materials:

- ex-pitch fibres swell less than ex-PAN fibres,
- 3D architectures have more dimensional stability than 2D architectures (to be noticed that needled felts exhibit non acceptable dimensional changes under irradiation),
- a high temperature treatment (≥ 2600°C) improves the thermal and dimensional stability of C/C materials.

All these results have to be confirmed by irradiation experiments on the selected materials under VHTR conditions. Indeed, past irradiation results on C/C are not so numerous and come mainly from “nuclear fusion” materials that are not tailored for VHTR applications. No real parametric study on the influence of the processing parameters (like matrix nature, fiber nature, fiber architecture, thermal treatment…) has been conducted which lead to difficulties to make the most of the past irradiation results. Moreover, there is a lack of data on the post-irradiation mechanical properties since it was not an issue for fusion program.

Oxidation effects

All the components are submitted, under normal conditions, to low oxidizing environment composed by helium gas with very small amount of water (P=40 to 70 bars, V=35 m/s, H_2O <10 µbar). Elsewhere, in case of accident these components will have to withstand air ingress at high temperature for several hours (see DML2.1-1 for technical requirements).

The normal conditions (low oxidizing atmosphere) might slightly affect the properties of C/C composites but there is a lack of data on the long term effect of low oxidizing atmosphere and some studies have to be conducted to evaluate the actual damage on composites.

Accidental conditions (air ingress), on the contrary, are known to be particularly damaging for C-based materials which are very sensitive to oxidation above 500°C. Oxidation tests in air should hence be performed to assess control rods life-time in case of air ingress.

A silicon based anti-oxidation protection could also be tested to limit the oxidation effects.

As for irradiation tests, oxidation tests have to be performed on the selected materials because the oxidation behavior depends strongly on the composite grade (matrix nature, fiber nature, fiber / matrix interface).

Design of the component

The design of the component is quite an important issue because it determines the material choice.

Indeed, in the field of composite materials, there are neither “off the shelf” materials, nor “standard material” properties.

The manufacturing parameters (fibre choice, fibre orientation, matrix choice, thermal treatment, thickness) have to be tailored to adjust the material properties and fulfil the technical specifications of the final component. These parameters might be different for each part of the control rod (co-axial tubes, lids, connecting system …) which might lead to the definition of different composite grades.

The design process of composite materials requires permanent links between the design step, the manufacturing step and the characterization step. Indeed, as there are no standard material properties, a first design of the component has to be made using estimated properties. After which, materials can be manufactured according to the manufacturing parameters defined in the first step and material properties can be measured. These measured properties can then be used to refine the design of the component.

Concerning the co-axial tubes of the control rods, one can notice that the manufacturing parameters have to be compatible with cylindrical structure.

Elsewhere, special attention should be paid to the connecting system between segments which could be the weakest link.

Some other points related to the qualification of the selected materials are also important issues that should be considered with special attention:

- The size effect and the geometry effect on material properties (links between flat and tubular specimens, links betweens small test specimens and full-scale components)
- The need for guidelines and procedures to qualify composites materials for nuclear reactor

5.2 Draft test program

As the budget is limited, it is suggested to focus on irradiation tests and eventually corrosion tests, considering that most of the properties of the raw materials should be provided by the manufacturer (thermal properties, mechanical properties).

The irradiation tests could be performed as piggy-backs within EXTREMAT irradiation campaign. The irradiation conditions have to be defined and should lie between 1 to 4 g.dpa and 800 to 1100°C. The following properties could be measured before and after irradiation: density, $\Delta L/L$, microstructure (cell parameters and crystallite size), thermal diffusivity in the temperature range [25-1000°C] and coefficient of thermal expansion in the temperature range [20-1000°C].

Concerning the oxidation tests, the first step consists in defining representative oxidation conditions. Indeed, C/C oxidation behavior depends on the gas composition but also on the gas flow and on the sample geometry. Some test could perhaps be performed within EXTREMAT program if there is enough material and if the oxidation conditions are suitable for VHTR application.

6 References

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