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Materials for the HTR**

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HTR-M WP2.1 – Carbon-Carbon composite control rods.
Report on discussions with manufacturers

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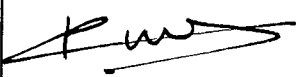
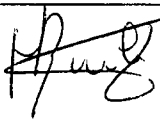
Carbon-Carbon Composites for control rods :

Report on discussions with manufacturers.

Deliverable 2.4

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Abstract

This report presents the results of CEA-Grenoble HTRM WP2 task on carbon-carbon (C/C) composites. The objective of this document is to report the discussions initiated with French C/C manufacturers for the procurement of composite pieces representative of the components of HTR (High Temperature Reactor) control rods. CEA was in charge of technical discussions with SNECMA and SGL. The proposals of these two companies for the fabrications of C/C tubes are compared and discussed in this document.

Key Words

Control rods, C-C composites

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I. Introduction and Specifications

This report presents the results of CEA-Grenoble HTRM WP2 task on carbon-carbon (C/C) composites.

The objective of this document is to give the results of discussions initiated with French C/C manufacturers for the procurement of composite pieces representative of the components of HTR (High Temperature Reactor) control rods. Mechanical testing of these elements were initially planned within the HTRM project.

CEA was in charge of technical discussions with SNECMA and SGL. The proposals of these two companies for the fabrications of C/C tubes are compared and discussed in this document. This report will be completed by the contribution of other partners who have planned to contact other foreign suppliers.

I.1 Background

The concept of the JAERI for the HTTR (High Temperature Test Reactor) control rods has been considered as a good guideline to specify to the different suppliers of C/C composite the geometrical characteristics of the components. The Japanese design for the control rod is illustrated by the figures 1 et 2 [1]. It consists of an outer and inner cladding tube, bolts and plugs, which are all made of C/C composite material. The outer diameter and length of the control rod corresponds to the HTTR core design : 133 mm and 3094 mm respectively. According to the concept, the rod consists of ten units which are connected in series using bolts and plugs. Between the outer and inner cladding tubes the annular compacts of the reactivity controlling material, boron carbide (B_4C), will be placed.

Three examples of C/C components elaborated in the frame of the JAERI program are illustrated in figure 3. 2D and 3D fiber textures and two grades AC-250 (Across Co.) and CX-270 (Toyo Tanso Co) have been considered in their on-going programs [2].

I.2 Requirements

CEA has presented to the composite manufacturers the following requests :

- supply of ten tubes with an external diameter of 113 mm and 4 mm thickness,
- supply of ten tubes with an external diameter of 75 mm and 7.5 mm thickness,
- supply of M8 and M16 bolts.

Concerning the material, we specified that the maximal operating temperature was 1600 °C. The selected grade has to support a tension stress of 30 MPa and a shear stress of 10 MPa.

We did not specify any accurate requirement related to the material evolution under irradiation excepting the control of activable element content (Cl, Ag,..).

Different mechanical tests were envisaged on these components :

- axial compression on tubes (buckling),
- diametrical compression on tubes or rings,
- flexure tests on bolts.

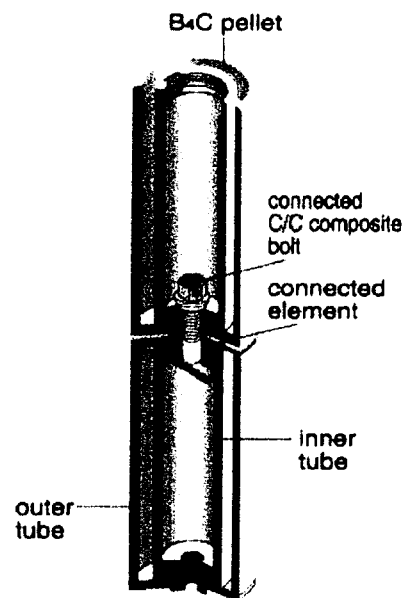


Figure 1 : Schematic view of the C/C composite control rod according to the JAERI design.

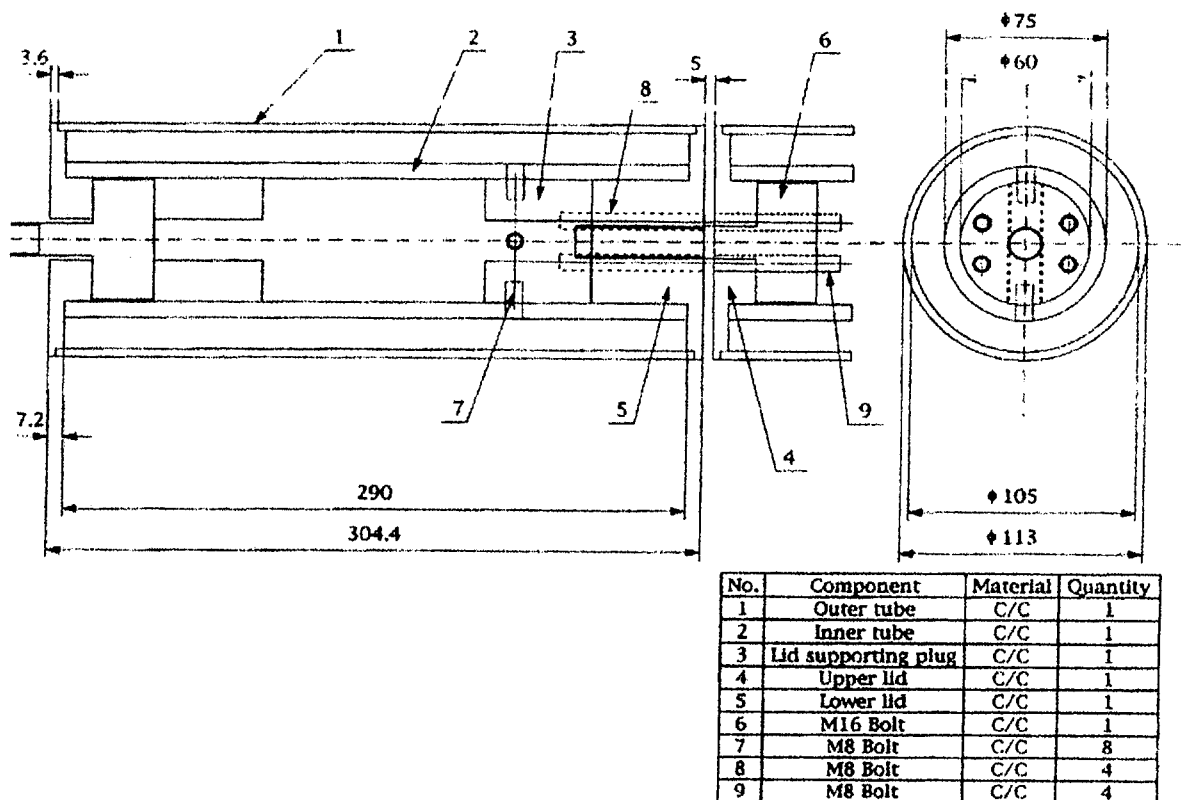
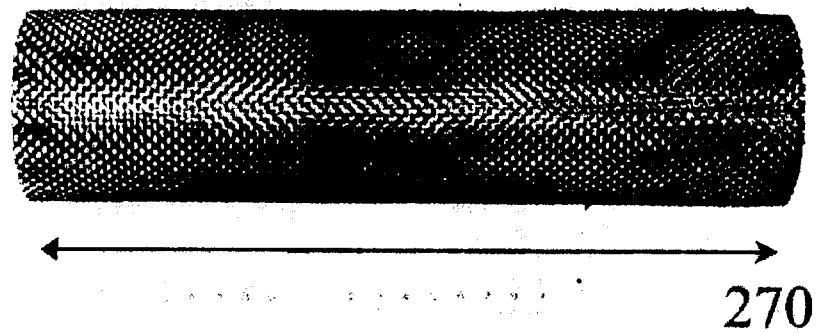
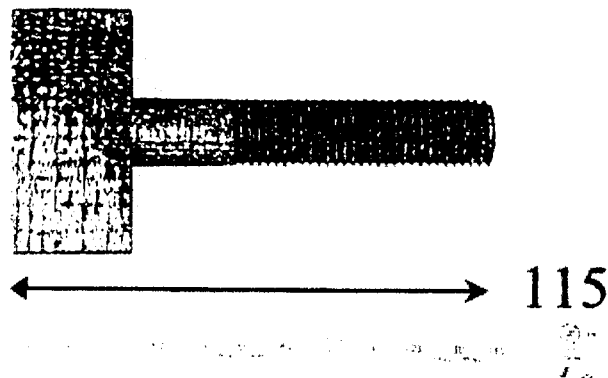


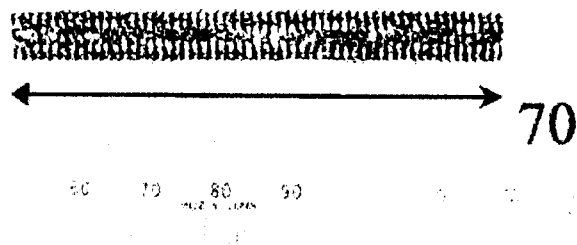
Figure 2 : JAERI concept for the control rod structure.



(a) Outer tube of control rod sheath(CX270)



(b) M16 bolt(AC250-2D)



(c) M8 bolt(AC250-2D).

Figure 3 : Example of C/C control rod elements tested by JAERI.

II. Identification of contacted persons

The contacted persons identified at SNECMA and SGL to initiate technical discussions on C/C materials were :

- SGL : Jean Paul Schmitt, SGL Carbon SA, 18 av. Marcel Cachin, BP 308, 38047 Saint Martin d'Hères, France jean-paul.schmitt@fr.sglcarbon.de, phone +33 4 76 25 96 55.
- SNECMA : Jean-Louis Limousin, Snecma Propulsion Solide, Les cinq chemins, F 33187 Le Haillan Cedex, France, phone +33 05 56 55 30 00 (Mr Limousin is now replaced by Mrs Fabienne Pothin)

III. SGL and SNECMA quotations.

Both SGL and SNECMA have positively responded to our technical requests. The manufacture of tubes or bolts is current and no technical development is required. During our discussions, we learned that SGL has been involved with past HTR projects (collaboration with FZJ-Jülich on C/C tubes) and that SNECMA has recently produced C/C tubes for JAERI.

III.1 SGL proposal.

SGL has proposed the grade SIGRABOND 2001G to meet our specifications. The fabrication of nuts and bolts is possible but was not quoted.

For the tubes, a quotation was proposed by email (June 3rd 2002) as follows :

- for 10 tubes ϕ 108/100 mm x 300 mm : 790 € per tube (total 7900 euros)
- for 10 tubes ϕ 73/58.6 mm x 300 mm : 885 € per tube (total 8850 euros)

The fabrication delay is 18 weeks, the proposed dimensions are slightly different to the requested specifications and correspond to standard dimensions at SGL.

III.2 SNECMA proposal.

SNECMA has proposed two quotations for C/C tubes with the grade N11. If the control rods must withstand temperatures greater than 1200°C and high fluences, a final graphitization at very high temperature (2500 °C) is recommended. As this process is expensive, this final treatment was proposed as an option.

The quotation was send on March 4th 2002. A copy is presented in annex 1:

A) without final graphitization :

- 10 tubes ϕ_{ext} 113mm, thickness 4 mm, length 300 mm : 24564 €
- 10 tubes ϕ_{ext} 75mm, thickness 7.5 mm, length 300 mm : 19115 €

B) with final graphitization :

- 10 tubes ϕ_{ext} 113mm, thickness 4 mm, length 300 mm : 56348 €
- 10 tubes ϕ_{ext} 75mm, thickness 7.5 mm, length 300 mm : 38595 €

The fabrication delay is 8 months + 1 month for the optional graphitization.

IV. Mechanical properties of SNECMA and SGL proposed grades.

The properties listed in this section were obtained from open literature or supplier technical documentations. These properties must be considered as “rough estimates” as the real properties of C/C tubes will strongly depend on the precise fiber structure, orientation, and also the matrix properties.

IV.1 SNECMA N11 material

SEPCARB N11 is a 3D composite made of PAN (PolyAcryloNitril) fibers reinforcement embedded in a matrix obtained by a Chemical Vapor Infiltration process (CVI). Infiltration is followed by a high temperature graphitization (leading to N11-012 and N11-052 grades) eventually followed by an additional densification (leading to the grades N11-011 and N11-051). Needling operation is achieved to obtain a reinforcement in the third direction.

The density ranges from 1.71 to 1.78 g/cm³.

The mechanical data obtained for N11 grades are presented in the following tables. Note that these data are given in the SEP documentation for plate components. The arrangement of fibers for the proposed tubular pieces has not been indicated by Snecma.

Young Modulus :

temperature (°C)	Young Modulus E							
	(GPa)							
	N11-011		N11-012		N11-051		N11-052	
	//	⊥	//	⊥	//	⊥	//	⊥
20	30	16	22	12	20	18	16	14
1000	30	16	22	12	20	18	16	14

Tensile strength :

temperature (°C)	Tensile strength R _m							
	(MPa)							
	N11-011		N11-012		N11-051		N11-052	
	//	⊥	//	⊥	//	⊥	//	⊥
20	75	32	50	20	54	35	38	27
500			50	24				
1000	90	38	60	28	70	42	50	32
1500			70	32	80	48		

Tensile rupture strain :

temperature (°C)	Rupture strain ε							
	(%)							
	N11-011		N11-012		N11-051		N11-052	
	//	⊥	//	⊥	//	⊥	//	⊥
20	0,40	0,35	0,40	0,35	0,44	0,38	0,39	0,35
1000	0,45	0,38	0,45	0,38	0,50	0,40	0,45	0,38

Compressive strength

temperature (°C)	Compressive strength R_{comp} (MPa)							
	N11-011		N11-012		N11-051		N11-052	
	//	⊥	//	⊥	//	⊥	//	⊥
20	100	80	100	80	100	100	90	90
500			100	80				
1000			120	95				
1500			140	110				

Shear strength :

temperature (°C)	Shear strength R_s (MPa)							
	N11-011		N11-012		N11-051		N11-052	
	⊥	//	⊥	//	⊥	//	⊥	//
20	26	32	18	20	30	30	19	20
500			20	20				
1000			23	24				
1500			25	28				

IV.2 SGL SIGRABOND 2001 G grade

SIGRABOND 2001 G is a grade developed to produce tubes or axi-symmetrical parts. The fibers texture is based on winded rovings. Different staking sequences are available : $[0^\circ/\pm 45^\circ/90^\circ]$, $[(+20^\circ)_{2x}, (+90^\circ)_{1x}]$, $[(+45^\circ)_{2x}, (+90^\circ)_{1x}]$, $[(+75^\circ)_{2x}, (+90^\circ)_{1x}]$. Its density is 1.56 g/cm^3

Mechanical properties obtained for this grade are scarce but some room temperature data were obtained from SGL booklet on composites :

- Young modulus $E = 25\text{-}30 \text{ GPa}$
- Flexural strength = $80\text{-}90 \text{ MPa}$
- Interlaminar shear strength $5\text{-}7 \text{ MPa}$

V. Discussion

Because only scarce data are available on mechanical properties of the selected composite grades, it is difficult to give a « best option » between SGL and SNECMA quotations. It can only be noted that the Snecma materials seems to have better shear resistance ($> 20 \text{ MPa}$ for N11-012) that could be the effect of the 3D fiber texture of this grade. The density is also higher for the Snecma grades. However, the lower interlaminar shear strength of SGL grade ($5\text{-}7 \text{ MPa}$) could be balanced during the step of components design.

Initially, it was planned to perform mechanical tests on 2 composite grades within the frame of HTRM project, but the program was re-assessed in 2002 and it was decided to focus more on bibliographic data collection rather than experimental work.

Nevertheless, the discussions with SGL and SNECMA allowed us to have a better view of their respective experience and possible involvement in the development of C/C tubes for a nuclear application :

- SGL appeared really “opened” to discussions and their quotation seemed “reasonable” for the production of 20 tubes dedicated to experimental work. SGL has a large experience of graphite production for nuclear reactors and therefore has the knowledge of specific constraints of the nuclear environment like the control of activable element impurities.
- SNECMA has proposed a very costly solution for the production of 20 tubes. The main reason lies in the fact that their capability of production greatly exceeds this demand. Technical discussions were not so easy as with SGL because of the confidentiality of many data (production process, mechanical properties). SNECMA seems to have some experience in the field of nuclear applications. Recently, SNECMA produced C/C tubes for the JAERI test program.

Representative people from both manufacturers made recently detailed presentations during the Technical Workshop on C & SiC composites for nuclear applications held at NRG-Petten, Netherlands (17-18 feb 2004). They were interested by the application of C/C composites for HTR core structures but seemed to be very sensitive to the confidentiality aspects. Basically, they stated that existing industrial grades of C/C could be currently selected and improved according to specific technical specifications.

References

- [1] M. Eto et al., Development of carbon/carbon composite control rod for HTTR – concept, specification and mechanical test of materials. JAERI-Research 98-003.
- [2] Ishiyama,-S.; Fukaya,-K.; Eto,-M. Journal-of-the-Atomic-Energy-Society-of-Japan. Oct. 1999; 41(10).

Annex 1 : SNECMA Quotation.

CEA
DRT-DTEN-SMP-LS2M
17, rue des martyrs
38054 GRENOBLE CEDEX 9

Bordeaux, le 4 mars 2002

Référence : FPI0260690A

A l'attention de Monsieur Raphael COUTURIER
Ingénieur Essais Mécaniques

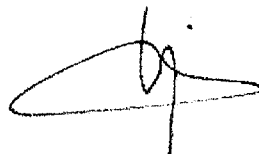
Monsieur,

Dans le cadre de votre application RCG, nous vous prions de bien vouloir trouver ci-après notre meilleure proposition technique et financière relative à la fourniture de tubes en carbone/carbone, conformes aux dimensions que vous nous avez communiquées.

Dans un 2^{ème} temps, nous vous communiquerons les prix de la visserie dès réception de votre définition.

Vous en souhaitant bonne réception et, restant à votre disposition pour tout complément d'informations,

Nous vous prions d'agréer, Monsieur, l'expression de nos meilleures salutations.



Jean-Louis LIMOUSIN
Chef de marché Développement Industriel

PROPOSITION TECHNIQUE ET FINANCIERE

Réalisation de tubes $\varnothing$ 113 et 75 mm pour application RCG

1. OBJET

Le CEA Grenoble recherche pour une application barre de contrôle sur le futur réacteur RCG, des matériaux C/C sous forme tubulaire.

Dans un premier temps cette proposition concerne la fourniture de tubes de longueur 300 mm destinés à une campagne d'essais mécaniques simples.

2. DOCUMENTS ET INFORMATIONS DE REFERENCE

Premières données techniques par mail CEA

- Dimensionnel: tubes $\varnothing$ ext 113mm long 300mm ép 4mm
tubes $\varnothing$ ext 75 mm long 300mm ép 7.5mm
- Température maximale : 1600°C
- Contraintes mécaniques : 30 MPa en traction et 10 Mpa en cisaillement

3. PRESTATION

CHOIX MATERIAU:

La géométrie des pièces d'une part, et notre expérience de production de matériaux pour l'industrie Nucléaire d'autre part (en particulier la fusion), font porter notre choix sur un matériau voisin du N11 livré pour les premières parois de Tokamaks.

La différence essentielle porte sur l'arrangement des fibres, cylindrique dans le cas des tubes, plutôt que plan pour les tuiles de divertors.

Si vos essais amènent le matériau à subir des températures supérieures à 1200°C et/ou des fluences importantes, alors, nous préconisons un traitement final à très haute température (>2500°C)

Ce traitement sera relativement onéreux car les capacités de nos moyens de production sont bien supérieures à la quantité objet de cette offre.

Ce traitement n'est peut-être pas indispensable dans un premier temps, c'est pourquoi nous vous proposons deux états de livraison optionnels en fonctions de la représentativité que vous souhaitez donner à vos essais :

- Etat non graphité
- Etat graphité après traitement thermique très haute température (>2500°C)

3.1. Tubes état non graphité

Pour un lot de 10 tubes $\varnothing$ ext 113 mm Longueur 300mm Epaisseur : 4mm

MONTANT:	24 564 € HT
-----------------	--------------------



Référence : FPI0260690A

Pour un lot de 10 tubes Ø ext 75 mm Longueur 300mm Epaisseur : 7.5mm

MONTANT: 19 115 € HT

3.2. Tubes état graphité

Pour un lot de 10 tubes Ø ext 113 mm

Surcoût opération de graphitisation : 31 790 € HT

MONTANT: 56 348 € HT

Pour un lot de 10 tubes Ø ext 75mm

Surcoût opération de graphitisation : 19 480 € HT

MONTANT: 38 595 € HT

Tous les prix d'entendent franco de port et d'emballage

4. DIVERS

4.1. Délais

- Tubes non graphités: le délai de livraison est de 8 mois ouvrables.
Il sera confirmé à réception de commande.
- Tubes état graphité: délai supplémentaire de 1 mois

4.2. Conditions de paiement

- Acompte 30% à la commande.
- Solde à la livraison
Règlements à 30 jours fin de mois.

4.3. Validité

Cette offre est valable jusqu'au 31 mai 2002