C/SIC COMPOSITES FOR PROPULSION APPLICATION

Suresh Kumar[1,2*1], Rajesh Chandra[2], Anil Kumar[2], N. Eswara Prasad[1] and L.M. Manocha[1]

[1]Defence Materials &Stores Research and Development (DRDO) Kanpur, India -200804
[2]Advanced Systems Laboratory (DRDO) Hyderabad, India -500058

Carbon fiber reinforced silicon carbide (C-SiC) composites are ideal materials for thrust vectoring control of missiles due to their high specific strength, erosion resistance and high temperature capability. Jet-vanes based thrust vectoring control is required in the initial phase of the launch where aerodynamic forces are insufficient to get required maneuverability. The environment experienced by the jet-vanes is very severe with typical gases temperature around 2500K at about 3-4 Mach; the exhaust gases contain hard tiny particles of alumina and results in severe erosion of jet-vanes. An indigenized technology based on liquid-silicon-infiltration method is developed for C-SiC composite jet-vanes. The jet-vanes have been tested and repeatedly performed successfully in solid propellant rocket motor. This paper describes the research efforts put for developing the technology and fabrication of the Jet-Vanes.

Keywords: Jet-vanes, 3D-stitched C-SiC composites, mechanical properties, thermal properties.

КОМПОЗИТЫ УГЛЕВОЛОКО – SiC ДЛЯ ПРИМЕНЕНИЯ В ДВИГАТЕЛЯХ

Suresh Kumar[1,2*], Rajesh Chandra[2], Anil Kumar[2], N. Eswara Prasad[1] and L.M. Manocha[1]

[1]Defence Materials &Stores Research and Development (DRDO) Kanpur, India -200804
[2]Advanced Systems Laboratory (DRDO) Hyderabad, India -500058

Композиты с углеволокном в карбид-кремниевой матрице (C-SiC) являются идеальным материалом для снарядов с управляемым вектором тяги благодаря их высокой удельной прочности, сопротивлению эрозии и высокой температуре использования. Управление вектором тяги необходимо на начальной фазе запуска снаряда, когда аэродинамической силы недостаточно для нужного маневрирования. Среда, в которой работают направляющие лопатки в сопле, весьма агрессивна; при температурах до 2500°K потока со скоростями 3-4 **M** газ может нести твёрдые мелкие частицы оксида алюминия, вызывающие эрозию.

Для получения композитных лопаток разработан управляемый технологический процесс, основанный на инфильтрации расплава кремния. Лопатки были успешно испытаны в условиях работы совместно с твердотопливным ракетным двигателем. Настоящая статья описывает исследования, направленные на технологию получения лопаток.

Ключевые слова: сопловые лопатки, 3D C-SiC композиты, мех. свойства, температурные свойства.

1.0 Introduction

Vertically launched missile systems require jet-vane based thrust vector control during the initial phase of the launch. The environment experienced by the jet-vanes is very severe with typical exhaust gases temperatures around 2500K at about 3 – 4 Mach velocity. C-SiC composites have received considerable attention as materials for jet-vanes, because of their superior strength, fracture toughness, and erosion resistance properties [1-3]. C-SiC composites are made using chemical vapor infiltration (CVI) of methyl-tri-chloro-saline vapors over heated carbon fibers and made to crack thereon depositing SiC [1]. CVI process is very slow and requires 1000's hours long continuous processing along with very precise control requiring sophisticated equipments. German Aerospace Center (DLR) has developed

[1] *Corresponding author Email: sureshtanwar@rediffmail.com*

liquid-silicon-infiltration (LSI) based C-SiC composites using the polymeric resins as carbon source, which is relatively fast [5]. In our laboratory, an indigenized technology based on liquid-silicon-infiltration method is developed for C-SiC composite jet-vanes using coal-tar pitch impregnation followed by silicon infiltration and chemical reaction. In LSI process, molten silicon infiltrates into the pores of carbon-carbon (C-C) preform developed through pyrolysis of coal tar pitch impregnated carbon fiber composites by capillary action and reacts with carbon to form SiC matrix. SiC provides oxidation and erosion resistance to the structure which is of prime importance for the jet-vanes applications [4-7]. Mechanical and thermal properties of the composites are required as design input for the jet-vanes design. There are many activities involved in the development of je-vanes like: optimization of process, characterization, machining, design and testing. This paper describes the most critical activities i.e. process technology, characterization and rocket motor testing. Issues like machining and design have been discussed in brief for completeness.

2.0 Materials and experimental procedures

2.1 Materials: High strength carbon fiber reinforcement in the form of woven fabric and tows were used to fabricate 3-D-stitched carbon fibrous preforms. Low quinoline soluble coal-tar pitch was used as carbon source for rigidization of preforms and high purity silicon metal of Indian Metals and Ferroalloys was used for siliconization.

2.2 Preform development: 3D-stitched carbon fibrous performs were prepared by stitching several layers of the 3k/8H satin woven carbon-fabric layers with 6k carbon fiber tows to impart third direction reinforcement.

2.3 Densification: 3D carbon fibrous preforms were rigidized by vacuum infiltration with coal-tar pitch at 200–300 °C followed by carbonization at 900-1000 °C and graphitization at 2500-2600 °C. Densification of porous Carbon- carbon was done by hot- iso- static- pressure- impregnation-carbonization (HIPIC) at 1000 bar and 800 °C in inert atmosphere to get C-C composite preforms of densities 1.55-1.60 g/cm^3. Siliconization process was optimized with respect to properties; the siliconization was carried out at 1450-1650 °C for 10 to 120 minutes. Schematic of the silicon infiltration process is shown in Figure 1. Sixteen C-C composite preforms were siliconized and factorial design of experiments was employed. Properties of the coupons were determined at each condition. Effect of siliconization conditions has been discussed in details by Suresh et al. [8].

2.4 Characterization: The C/SiC composite coupons processed at different conditions were cut according to ASTM standards and were tested for mechanical and thermal properties. Flexural strength under three point bending load was determined as per ASTM C-1341 while tensile strength as per ASTM C-1275-00 using universal testing machine (Instron, model 8801). Thermal diffusivity and coefficient of thermal expansion were determined as per ASTM E-1461 and ASTM C-1470-00 respectively. The properties were found to be the best for the coupons siliconized at 1650 °C, 120 minutes. Therefore jet-vanes were siliconized at 1650 °C, 120 minutes. Several C-C

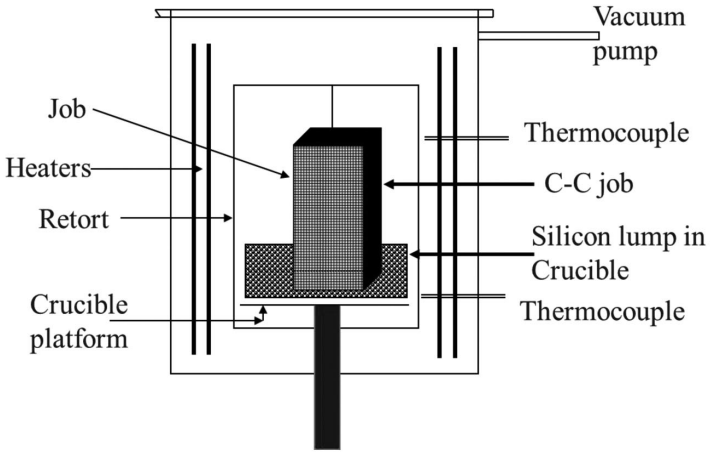

Fig. 1. Schematic of silicon infiltration
Рис. 1. Схема пропитки кремния

preform blocks were machined to near net shape of jet-vanes and were kept in a graphite crucible along with lumps of silicon metal in a vacuum furnace, shown in fig. 1. Silicon infiltration was carried out.

3.0 Results and discussion

3.1 Physical properties: Silicon uptake and density of the C-SiC composites after siliconization were measured. Silicon uptake was observed in the range of 38-44% for the coupons siliconized at different conditions. Uptake is found to be increased with time and temperature. It was also observed that content of SiC in the matrix increases with time and temperature. The reaction of carbon matrix and molten silicon is instantaneous but further reaction is dominated by diffusion of silicon through SiC layer. Therefore uptake of Si and formation of SiC increases with time and temperature. Density of the C-SiC composite coupons and jet-vanes siliconized at 1650°C, 120minutes varies in the range 2.15-2.25g/cc uniformly while the coupons siliconized at other conditions show higher variation w.r.t. silicon uptake and density. The experimental C-SiC composite coupons siliconized at 1650°C, 120minutes along with jet-vanes were cut into standard sizes for mechanical and thermal characterization.

3.2 Mechanical properties: Using the design of experiments (DOE) it was established that mechanical properties improve with siliconization time and temperature. Therefore for detailed analysis coupons siliconized at 1650°C, 120minutes were chosen.

3.3 Flexural strength: Flexural strength was determined for 15 specimens. Flexural strength is found to be in the range 140-203MPa while strain to failure is in the range 0.003-0.0035. Average strength and standard deviation were found to be 173.4 MPa and 17.8 MPa respectively.

Ceramic materials are sensitive to initial heterogeneities (e.g., inclusions, porosities). These imperfections are created during the fabrication of the material and are usually randomly distributed within the material or at the surfaces, which lead to scatter in the failure load. The scatter in bending properties of 3D-stitched-C-SiC composites is attributed to three factors, i.e. characteristic non-uniform shrinkage of C-C preform blocks, fiber-matrix interface, and location of the third-direction reinforcement carbon-fiber tow in the test specimen. It is well known that residual pores/ non-uniform gaps in the texture are considered as a kind of defects and act as failure source. The specimens which failed at lower loads than usual were examined under stereo-microscope, optical microscope and scanning electron microscope. It was observed that the specimen offers lower strength than usual if any of the following existed: i) lager diameter pore (>100 ìm) in span length, ii) third direction stitched at the edge of the specimen, iii) interfacial debonding. To obtain reliable design inputs the specimens must be prepared and tested as per STM standard and the results to be interpreted suitably. ***3.4 Tensile strength:*** Tensile strength was found to be in the range 75-102MPa with average strength of 90MPa and strain to failure is in the range of 0.0078-0.0092. Tensile strength measured on dumbbell as well as on straight specimen was found to be similar. All specimens failed in the respective gauge lengths. The variation in tensile strength values was analyzed and it was concluded that the factors responsible for variation in flexural strength are responsible for variation in tensile strength. Further details can be extracted from Suresh et al. [8].

The scatter in mechanical properties of 3D-stitched-C/SiC is attributed to the characteristic non-uniform shrinkage of C–C, interfacial situation between fiber and matrix, and location of third-direction reinforcement carbon-fiber tow in the test specimen. It is well known that residual pores/non-uniform gaps in the texture are considered as a kind of defects in the ceramic composites and act as failure source. In 3D-stitched-C-SiC composites, there are small pores which lie between warp and weft of fabric (of the order of few microns) at cross-over points and the larger pores between two fabric layers (up-to 300 microns). This fact was confirmed by porosity data from mercury porosity-meter testing. Pores are found in the wide range of 0.001–324 microns diameter. During carbonization and graphitization coal–tar pitch shrinks on to the fabric layers. The fabric layers do not shrink with carbonization of pitch because of third direction carbon fiber reinforcement. Due to the limitation of the LSI process and structure complexity of 3D-stitched-C-SiC, it is very difficult to fill all the pores completely. Specimen offer lower strength than usual if any lager diameter pore comes in span length. It has also been observed that the properties vary with the composition of the matrix. The composites, where siliconization was carried out at higher temperature and for longer durations the SiC content was found to be higher as compared to the ones which were siliconized at lower temperature. The mechanical properties were found to increase with siliconization time and temperature.

3.5 Thermal properties: Thermal properties of such composites are highly dependent on the testing direction. As a design input these have to be available for both the directions i.e. in in-plane and through thickness directions.

3.5.1 Thermal diffusivity: The in-plane thermal-diffusivities (II) of the C-SiC composite blocks are found to be two-three times higher than those in the through-thickness direction (⊥). It varies from 77 at room temperature to 14.7 mm^2/s at 1500°C in in-plane and 36 - 6.1 mm^2/s in through-thickness direction. Thermal-diffusivity decreases with increase in testing temperature for all the C-SiC composite blocks and in both the testing directions. Thermal diffusivity decreasing nature of these composites is due to similar nature of the basic constituents of these composites [8]. That is thermal diffusivity of the carbon fibers, SiC, and silicon metal decreases with testing temperature. Different aspects of the thermal diffusivity and its dependence on the process parameters are published elsewhere [9].

3.5.2 Coefficient of Thermal Expansion (CTE): CTE was also investigated in in-plane (II) and through-thickness directions (⊥) from room temperature to 1050°C. The in-plane CTE was found to vary in the range 0.5-$2x10^{-6}$/°C, while the through-thickness CTE in the range 1.5- $4x10^{-6}$/°C depending on the siliconization conditions. Extensive microstructure studies were carried out to understand the thermal expansion behavior of the composites. Above 600°C steep expansion is observed due to de-bonding of the third direction fibers and positive expansion of carbon fibers. Third-direction stitching helped greatly to contain the CTE much lower than the C-C and CVI based C-SiC composites. The information was used as design input for designing of the jet-vanes thickness, insulation and jet-vane metal interfaces. The different aspects of the coefficient of thermal expansion and its dependence on the process parameters are published elsewhere [10]. Summary of the properties generated and their comparison with the materials developed is given in Table 1.

Table 1

Comparison of properties with material developed at DLR, Germany [1, 5, 7**]**

	Unit	Present study	DLR, Germany
Fiber content	Vol.%	40-42	-
Density	g/cm^3	2.2-2.4	2.4
Flexural strength	MPa	160-240	180-200
Tensile strength	MPa	70-100	80-190
Young's modulus	(GPa)	40	60
Strain to failure	%	0.15-0.20	0.15-0.35
Thermal diffusivity	mm^2/s	∥ 75-15 ⊥35-8 (25-1500°C)	-
CTE	/°C	∥ $1x10^{-6}$ ⊥$1.5\text{-}2.0x10^{-6}$ (25-1500°C)	∥ $-1\text{-}1x10^{-6}$ ⊥$2.0\text{-}5.0x10^{-6}$ (25-1000°C)

4.0 Applications of C/SiC composites

As mentioned above, C/SiC composites are used for several applications like hot-structure, propulsion products, leading edges and nose tip etc. Jet-vanes used for the thrust vectoring application for the advanced rocket systems are very critical. In the subsequent sub-sections some details of the jet-vane fabrication and testing is given.

4.1 Jet-vane fabrication and testing: Several jet-vanes were siliconized. Silicon uptake varies from 43 to 46% while gain in density varies from 0.67-0.72 g/cm^3 consistently. The final density was found to be 2.3 g/cm^3 (± 0.05%).

4.2 Machining: Due to the presence of SiC matrix the C-SiC composites are very hard and cannot be machined using conventional techniques and tools. The machining is usually carried out in two steps.

i) At C-C composite preform block level where bulk of the material is removed,

ii) After siliconization the jet-vanes were machined using diamond wheel grinding and Electrical Discharge Machining (EDM) wire cutting.

4.3 NDT Characterization: Nondestructive testing (NDT) studies were carried out to qualify the jet-vanes for testing under rocket motor exhaust. Interior micro-cracks and low density zones were investigated. X-ray images of some jet-vanes siliconized are shown in Figure 2. De-lamination and micro-cracks free jet-vanes were qualified for testing. Now, the indigenous process has been standardized and rejection rate has been reduced to less than 5% of the processed jet-vanes. Few jet-vanes have to be tested using computer added tomography before acceptance.

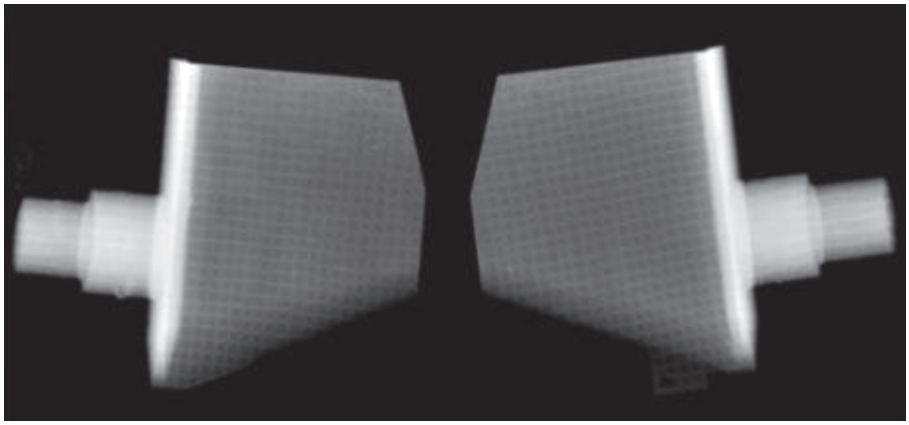

Fig. 2. X-ray images of qualified jet-vanes
Рис. 2. Рентгеновское изображение сопловой лопатки

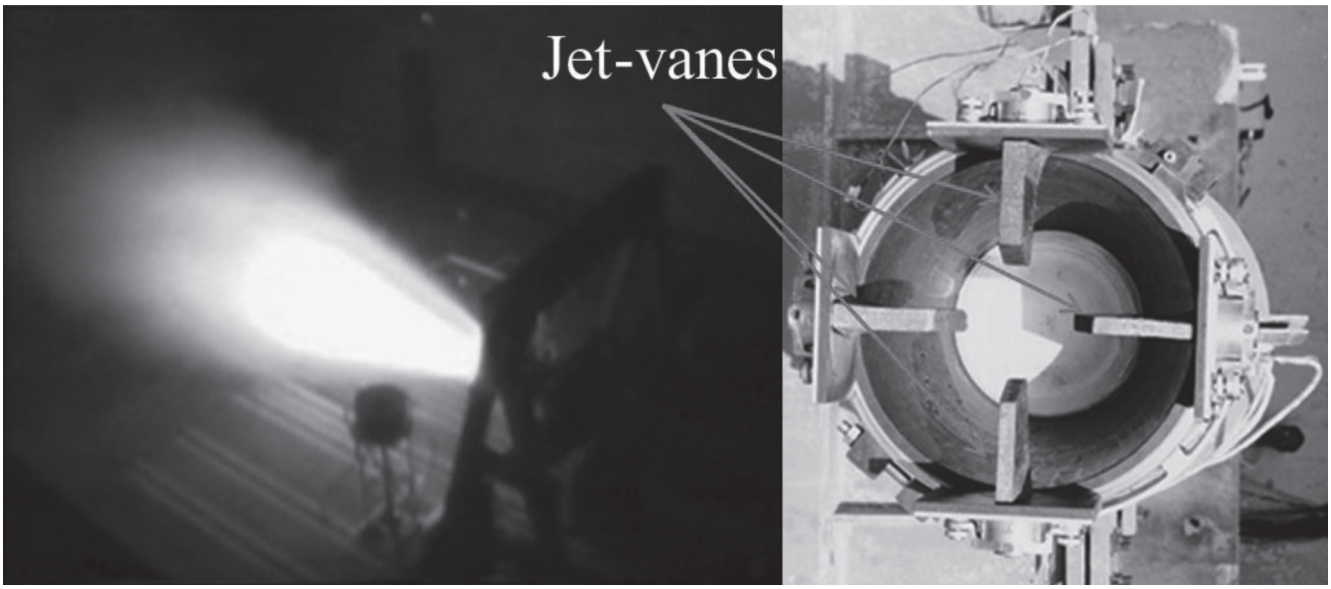

Fig. 3. Jet-vanes testing (static test)
Рис. 3. Испытания сопловой лопатки (статика)

4.6 Jet-vanes testing under rocket-motor exhaust: Jet-Vanes were tested in the plume of SRM. The SRM was loaded with the composite propellant composed of hydroxyl-terminated poly-butadiene, aluminum powder (17%, w/w) and ammonium per-chlorate (oxidizer) and some other additives. Using a special fixture four Jet-Vanes were held at 90° w.r.t. each other in the SRM plume. The plume hits the leading edge of the Jet-Vane at 0° for 8 s; the plume is parallel to the fabric layers and perpendicular to the third direction (reinforcement) stitches. The

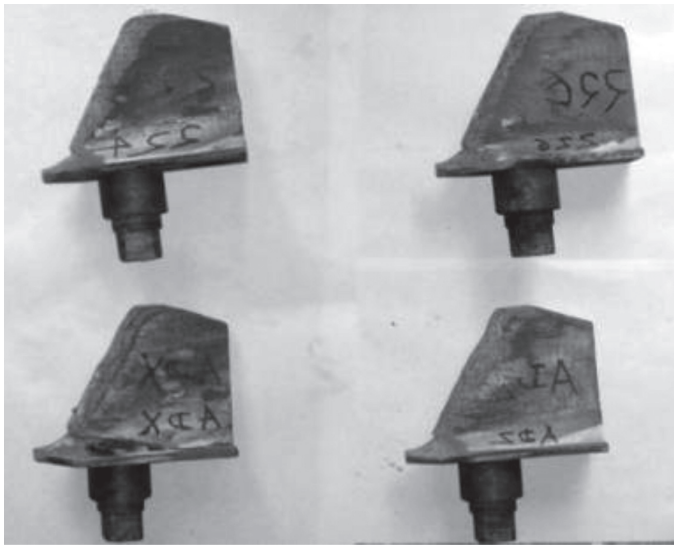

Fig. 4. Tested jet-vanes under rocket-motor exhaust
Рис. 4. Сопловая лопатка после нахождения в продуктах сгорания твердотопливного двигателя

velocity of the exhaust gases was of the order 3000 m/sec and temperature, of the order of 2500 °C. A set of 4 jet-vanes was used for testing; a picture of the actual test which was taken shown in Figure 3**.**

The jet-vanes have sustained the mechanical and thermal loads. The tested jet-vanes were retrieved from the rocket motor and analyzed for the erosion and weight loss. Weight loss was observed in the range of 6-7 %. Erosion was observed at leading edges of the jet-vanes which were facing the exhaust (Figure 4). The bodies of jet-vanes were found intact and there was no structural damage. Also no surface cracks were observed. Erosion rate was found to be consistent in the range 1.0- 2.5 mm/s for all the tested jet-vanes, which is well within the design requirements [11].

5.0 Conclusions

A simple indigenous technology for the C-SiC composite jet vanes has been developed. The jet-vanes performed successfully in solid propelled rocket motor tests. This indigenous technology initiative effort has also resulted in realization of C-SiC composite products for erosion resistant throat-inserts, hot gas-valves, leading edges and nose tip of the hypersonic technology demonstration vehicle.

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