한국추진공학회 2007년도 춘계학술대회 논문집 pp.185~188 2007 KSPE Spring Conference

C/SiC 복합재료의 내열성능 평가

김연철

Performance Evaluation of C/SiC Composites

Yun Chul Kim

ABSTRACT

The main objective of this research effort was to develope the performance of C/SiC composites manufactured by LSI (Liquid Silicon Infiltration) method for solid and liquid rocket propulsion system and ensure the performance analysis technique. The various carbon preform were manufactured by filament winding, tape rolling, involute layup and stack molding process. For the best performance of thermal and mechanical properties, many process conditions were tested and selected by varying preform, the content of SiC, temperature, impregnation resin and chemical vapour reaction. In conclusion, the high performance and reliability of C/SiC composite were proved for solid and liquid rocket propulsion system. And the performance analysis technique related to mathematical ablation model was originated.

초 록

액체 및 고체추진기관의 내열부품으로 사용하기 위하여 Liquid Silicon Infiltration(액체 실리콘 함침) 공정이 적용된 C/SiC 복합재료를 개발하였다. 탄소섬유 및 탄소직물을 사용하여 필리멘트 와인딩, 테이프 롤링 및 인벌루트 적층 공법이 사용된 다양한 탄소 프리폼이 제작되었다. 내열 부품으로써의 열구조 성능을 극대화시키기 위하여 SiC 함유량, 열처리 조건, 수지 및 기상 함침 조건을 변화시키면서 시편을 제작하고 평가하였다. C/SiC 복합재료를 액체 및 고체추진기관의 내열부품으로 사용하기 위하여 연소시험을 수행하였으며 내열 성능 해석을 위한 수학적 삭마 모델이 개발되었다.

Key Words: C/SiC(탄소/실리콘카바이드), Liquid Rocket Engine(액체로켓엔진), Solid Rocket Motor(고체로켓모타), Ablations(삭마), Liquid Silicon Infiltration(액체 실리콘 함침법), CFRP(탄소섬유보강 복합재료)

1. 서 론

In recent years, there has been a surge of interest in the design, manufacturing and testing of Carbon/Silicon Carbide (C/SiC) composites for a number of aerospace and

* 국방과학연구소 기-4-3
연락저자, E-mail: dendrite@hanafos.com

ground based applications. The potential applications of C/SiC in the aerospace industry include combustor liners, exhaust nozzles, a number of other aircraft gas turbine and space propulsion components. The ground-based applications of these materials include radiant burners, hot gas filters, high-pressure heat exchanger tubes and combustor liners in industrial gas turbine engines. At present, the majority of the approaches for the manufacturing of continuous carbon fiber reinforced ceramic matrix composites are based on fabricating single or multiple pieces **[1-3]**.

In order to improve the oxidation resistance and thus the application lifetime of these composites, research has been exerted on using ceramics instead of carbon as the matrix material. Silicon carbide is particularly suitable as a matrix material due to its high oxidation resistance, its superior temperature and thermal shock stability and its high creep resistance. Practically, similar manufacturing techniques can be used for the silicon carbide matrix formation of C/SiC composites as for the manufacture of carbon/carbon composites. Since the Liquid Silicon Infiltration Process (LSI) has been developed as cost effective new manufacturing for reentry vehicle components, investigations were first concentrated on basic material properties evaluation which also includes intensive testing in various arc jet facilities. As soon as a fundamental understanding of oxidation and erosion mechanisms was achieved, further efforts focused on real reentry flight testing and advanced design concepts for hot structures were made.

2. Backgrounds

2.1 Manufacturing process of C/SiC

Fig. 1 gives an overview of the LSI-process which can be split into three major steps. The fiber preform fabrication starts with the manufacture of carbon fiber reinforced plastic composites with polymeric matrices of high carbon yield. Normally, commercially available resins like phenolic or other aromatic polymers are used to fabricate laminates by common CFRP techniques like resin transfer molding, autoclave, warm pressing or filament winding. After curing, the composites are post-cured for the complete polymerization of the matrix (Figure 1). Subsequently, the CFRP composites are pyrolysed under inert atmosphere (e.g. nitrogen or vacuum) at temperature beyond 900°C to convert the polymer matrix to amorphous carbon.

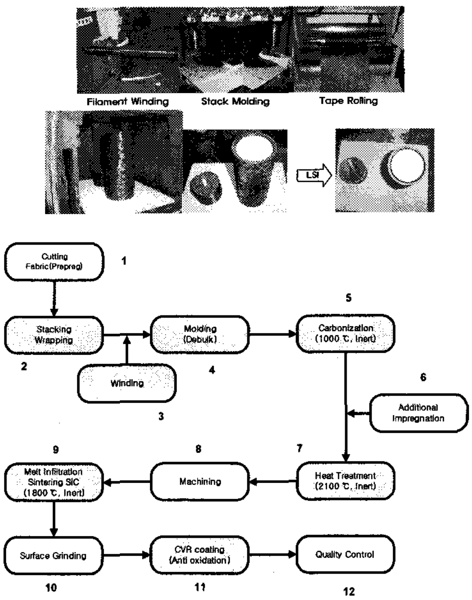

Fig. 1 The technological manufacturing process of C/SiC

2.2 Determination of oxidation reaction rates

Isotropic materials under high temperature consists of three phase: initial carbon fiber phase(a), SiC matrix phase(b), new solid SiO_2 phase(p) and gas phase(g) inside pores, and

$$\varphi_a + \varphi_b + \varphi_p + \varphi_g = 1 \quad (1)$$

Fig. 2 shows a scheme of such a periodic structure for a four phase. Let us consider a model shape for the phases inside the periodic cell. The pore is assumed to be a cube and the carbon fiber and SiC matrix phases are hollow cubes; we call this the cubic model.

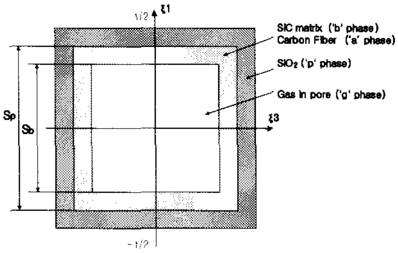

Fig. 2 Model of periodic cell of C/SiC under high temperature

As established the rate of surface ablation is described by the function J, which is connected to the linear rate of motion of the phase interface. For cubic pore Dimitrienko derive the expression for J.

$$J = J_0 \varphi_g^{\gamma} exp(-\frac{E_a}{RT}) \quad , \quad J_0 = \frac{6}{l_0} \frac{p_e}{\sqrt{RT}} \quad (2)$$

The cubic model gives a value of the coefficient γ=2/3. Experimental data are described more accurately with the value γ=1 which was considered.

The mass transfer equation for C/SiC under high temperature has the form

$$\rho_a \frac{\partial \varphi_a}{\partial t} = -J \quad , \quad \varphi_p = (\varphi_a^0 - \varphi_a) \frac{\rho_a}{\rho_p} (1-\Gamma) \quad (3)$$

For nonisothermal conditions, when the temperature varies with time with a constant heating rate, β=dT/dt, eq. (2) is represented as follows

$$\frac{\partial \rho_{c/sic}}{\partial T} = -\frac{1}{\beta} \frac{J_0}{\rho_{a,b}} \Gamma \cdot (\rho_{c/sic} - \rho_{c/sic}{}^{\infty}) \, exp(-\frac{E_A}{RT}) \quad (4)$$

On solving equation (4), we get

$$\frac{\rho_{c/sic}(T)}{\rho^0{}_{c/sic}} = 1 - \Gamma + \Gamma \cdot exp\left[-\frac{J_0 \cdot \Gamma}{\rho^0{}_{c/sic} \cdot \beta} \cdot \int exp(-\frac{E_a}{RT}) dT \right] \quad (5)$$

2.3 Thermal and oxidative ablation model

The behavior of different C/SiC composites in dry oxygen has already been extensively studied. It appears that it will strongly depend on the nature of the carbon and the SiC. Hence C and SiC will react in the composite with O_2 according to the following reactions:

$$2C(s) + O_2(g) \rightarrow 2CO(g) \quad (6)$$

$$SiC(s) + \frac{3}{2} O_2(g) \rightarrow SiO_2(s) + CO(g) \quad (7)$$

It must be noted that reaction (7) is valid only if the partial pressure of O_2 is high enough to have the passive oxidation regime. In this case, the oxidation of SiC leads to the formation of a protective silica film which will further limit the oxidation of the carbide.

On the contrary, a volatile non passivating oxide is formed at sufficiently high temperatures and low partial pressure of oxygen according to:

$$SiC(s) + O_2(g) \rightarrow SiO(g) + CO(g) \quad (7)$$

Reaction (7) corresponds to an active oxidation behavior characterized by a loss of weight.

3. Experiments

In order to investigate the influence of process parameters on the thermo-physical properties of C/SiC, samples of various sizes were cut from C/SiC plates which were manufactured according to the LSI-process. Phenol resin, Carbon fibers and Graphite fibers were used. At first CFRP plates were processed by autoclave technique. Then, the CFRP plates with a fiber volume content of roughly 60% (58 ~ 64%) were pyrolysed to C/C at 900 °C or optionally at 1700 °C. Some specimens were annealed above 2200 °C in an inductively heated graphite furnace in N_2 atmosphere for 2hr. In the last step the C/C templates were infiltrated with liquid silicon at 1700°C to form C/SiC. Proof or overstress testing a component has been obtained by multiple tests of C/SiC materials in TGA, arc plasma test facilities, Liquid Rocket Engine, Solid Rocket Motor.

3.1 Thermogravimetry analysis (TGA)

TGA curves recorded under air atmospheres. The reaction is initiated at a temperature of between 400℃ and is substantially complete when the temperature has risen above 1200℃.

3.2 Supersonic torch test (SST)

The STT is a small-scale, liquid-fueled rocket motor burning a mixture of kerosene and oxygen. The maximum ablation rate was measured at the center of the crater relative to an average of five points measured on the surface away from the area affected by the exhaust plume. The data acquired during the experiments included peak erosion.

Table 1. Ablation result of SST

Process diagram	Ablation result
C/P^1→HT1000→IPi^2→HT2200→LSI (65/5/20/10)	0.5 mm/sec
C/P^1→HT1000→IPi^2→HT2200→LSI(30/10/55/5)	No erosion (120 sec)
C/P^1→HT1000→IPi^2→HT2200→CVR→LSI(30/10/55/5)	No erosion, crack
C/P^1→HT1000→IPi^2→HT2200→LSI→CVR(30/10/55/5)	No erosion (120+60 sec)
C/P^1→HT1000→IPi^2→HT2200→LSI→CVR(65/5/20/10)	0.1 mm/sec

3.3 Liquid rocket engine

After 120 seconds steady burning, a thin silica layer was formed at the surface of the C/SiC composite combustion tube and the throat diameter did not increase and the silica surface layer did not crack and drop.

3.4 Solid rocket engine

The temperatures of combustion liner slightly increase during the burning. But the temperature of the steel case did not increase. At the end of the firing (10 sec), temperatures of nozzle throat and steel case are respectively equal to 560°K and 300°K. The temperature distribution of exit cone show that the temperature of exit cone surface approach to 1200K at the end of the firing time (10 sec). But the steel case of exit cone did not over 400K. We did not find any other crack in nozzle component. The white solid films, which are the result of melting of SiO_2 and Al_2O_3 were founded in the surface of exit cone.

4. Results and discussion

This work is for the development of high performance Carbon/Silicon carbide (C/SiC) composites using Liquid Silicon Infiltration (LSI) technology. C/SiC composites are interesting materials for an increasing number of applications in the aerospace industry as well as many others.

참 고 문 헌

1. Y.C.Kim, et al., Method for manufacturing carbon/silicon carbide composite, US Patent, US6838120(2005)
2. Y.C.Kim, et al., Method for manufacturing carbon/silicon carbide composite, FR Patent, FR 2820737 (2005)
3. V. I. Trefilov, Ceramic- and Carbon-Matrix Composites, Chapman & Hall (1995).