Development of Three Dimensional Composite with Extremely Low Thermal Expansion Properties

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Three dimensional carbon fiber reinforced carbon (3DC/C) composites have been used for rocket motor nozzle parts and other applications requiring heat-resistant properties for about ten years. We have developed two types of fabrication process of 3DC/C, the HIP carbonization process, and the large nozzle 3DC/C fabrication process. 3DC/C manufactured from these fabrication techniques has been applied for the C/C rocket nozzle throat. 3DC/C composites have another important characteristic of low thermal expansion. Three dimensional composites with extremely low thermal expansion properties have been newly developed by utilizing the thermal characteristics. This paper reports fabrication processes and properties.

1. Introduction

The carbon fiber reinforced carbon (C/C) composites are lightweight structural materials which, if placed in a non-oxidizing atmosphere, have high strength in the very high temperature region above 2 000°C. Using this property, its uses are increasing as a refractory furnace material, racing brake material and rocket nozzle material. The authors have developed a rocket nozzle throat material using three-dimensional C/C (hereinafter called 3DC/C) and, through this development, have established technology for the nozzle material. [(1), (2)]

The manufacturing method developed by IHI AEROSPACE CO., LTD. is based on the HIP (Hot Issostatic Pressing) process and can make high-density C/C. The rate of porosity can be reduced to a level below 5%, which is unattainable with the conventional atmospheric carbonizing process. In this development, a novel composite having very low thermal expansion characteristics was successfully made by impregnating metal aluminum into the pores of 3DC/C.

This article introduces its prospective uses in the future in the main and including its thermal expansion characteristics.

2. 3DC/C

2.1 Manufacturing method of 3DC/C

Before describing the extremely low thermal expansion three-dimensional composite, 3DC/C is introduced, which is the base material of this material development. 3DC/C was applied to the solid rocket booster (SRB-A) of the H2A rocket and the nozzle throat of the M-V rocket and gave good results. Its appearance is shown in **Fig. 1**. Because the nozzle throat is rapidly heated in a temperature environment of 2 000 to 3 000°C, its materials are required to be excellent in thermal shock properties. C/C reinforced in three dimensions by carbon fiber is confirmed to exhibit performance greatly superior to that of graphite materials.

There are various manufacturing methods for C/C; however, the common method is to manufacture it via CFRP (Carbon Fiber Reinforced Plastics). **Figure 2** shows the basic process flow of 3DC/C manufacture by this development. A feature is the carbon fiber

Fig. 1 C/C composite rocket nozzle (unit : mm)

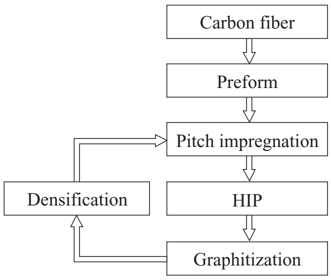


Fig. 2 Fabrication process of 3DC/C nozzle throat

woven in three dimensions into a preform (**Fig. 3**) which is subsequently subjected to repeated cycles of carbonization and graphitization under a high pressure of 98 MPa to attain high density. The density of the obtained 3DC/C increases with the number of densification cycles and can attain a level of 2.0 g/cm^3 in the end. **Figure 4** shows the bulk density versus the number of densification cycles.

It is very important for nozzle materials to be dense and homogenous. The HIP manufacturing method by this development is thought to be one of the most suitable

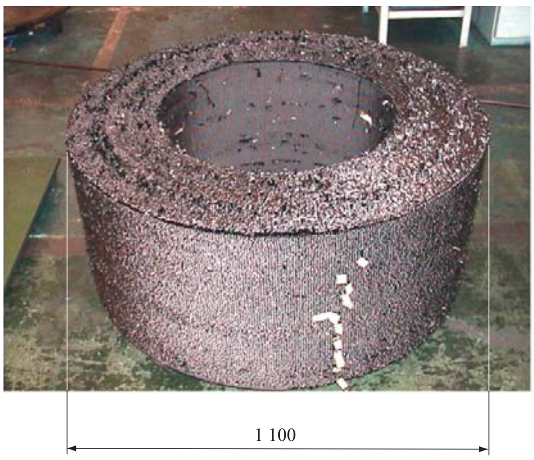


Fig. 3 3D carbon fiber preform (unit : mm)

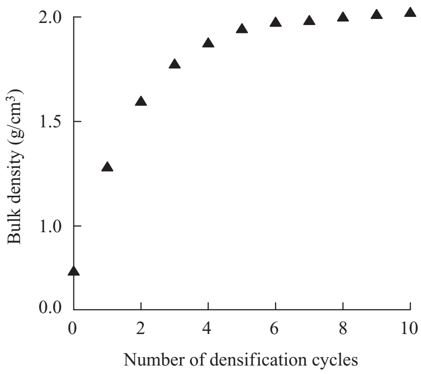


Fig. 4 Bulk density vs. number of densification cycles

manufacturing methods.

2.2 Features of 3DC/C

A major feature of 3DC/C is that it exhibits negative thermal expansion characteristics from room temperature to 800ºC. **Figure 5** shows the temperature dependence of the thermal expansion coefficient. This results from the structure of the carbon fiber and means that thermal contraction occurs as the temperature increases. The reason why the thermal expansion characteristics are negative is thought to be because the bond between carbon atoms in the carbon fiber used in 3DC/C is extremely strong.(3) The thermal expansion characteristics turn positive beyond 800ºC, but are still as small as 1×10^{-6}/ºC, even at 2 000ºC. No difference is observed in the thermal expansion characteristics between the axis directions (R, C, Z) of 3DC/C. Therefore, the material is thought to be substantially isotropic.

3. Three-dimensional composite with extremely low thermal expansion

3.1 Manufacturing process

For 3DC/C, its Rate of Porosity can be changed by controlling the Densification Cycle in the manufacturing process. **Figure 6** shows the rate of porosity versus the number of densification cycles.

As shown in **Fig. 5**, it is known that 3DC/C exhibits negative thermal expansion characteristics from room temperature to 800ºC. A material almost free of pores can be made by impregnating the pores with aluminum under high pressure by high-pressure casting (under conditions of 750ºC and 100 MPa). **Figure 7** shows the optical microstructure of the extremely low thermal expansion material.

As to compressive properties, the material is strengthened to show a compressive strength about 1.5 times the matrix C/C. The coefficient of thermal expansion shows an almost constant value in the range from room temperature to 100ºC, but can be changed between -4×10^{-7}/ºC to 2×10^{-6}/ºC. The minimum

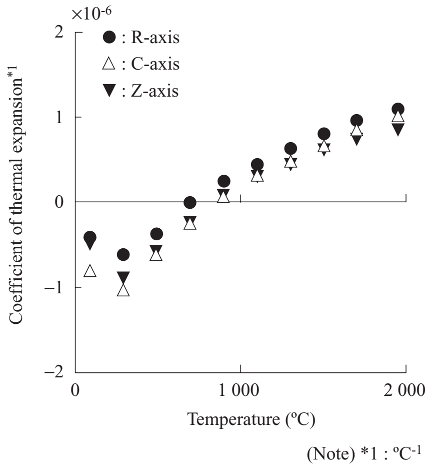


Fig. 5 Coefficients of thermal expansion vs. temperature

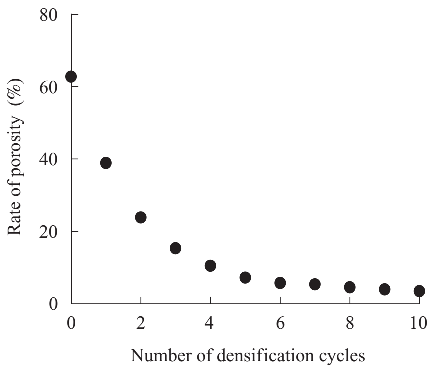


Fig. 6 Porosity vs. number of densification cycles

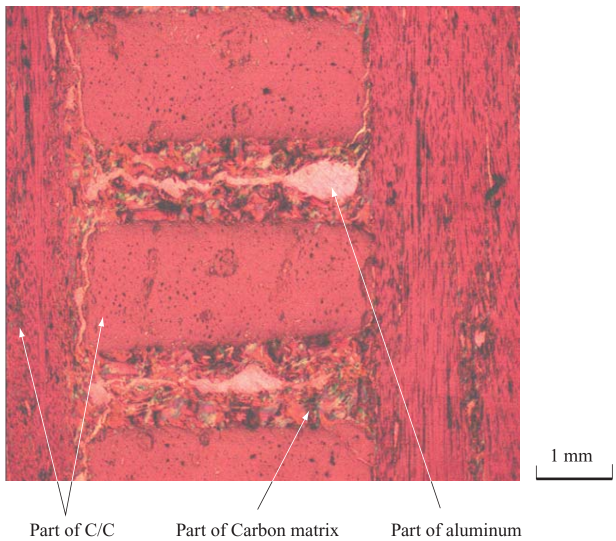


Fig. 7 Optical microstructure of 3D low C.T.E. composite

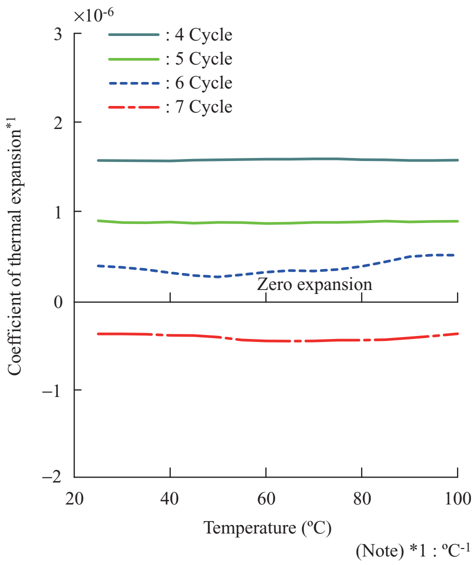


Fig. 8 Temperature dependency of C. T. E. (3D low C. T. E. composite)

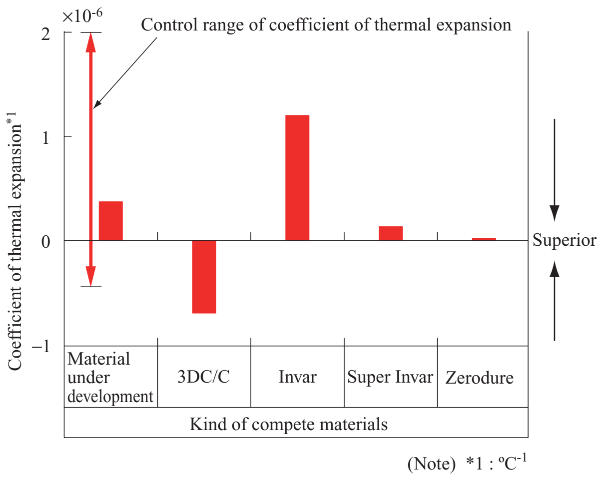


Fig. 9 Comparison of C. T. E.

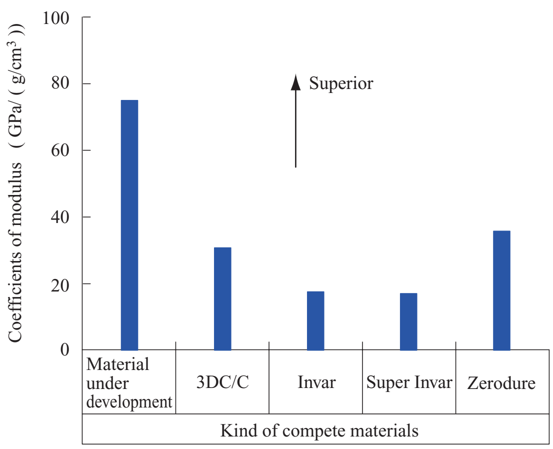


Fig. 10 Comparison of coefficients of modulus

magnitude of thermal expansion is 3.7×10^{-7}/ºC, or nearly zero. **Figure 8** shows the temperature dependence of the coefficient of thermal expansion of the extremely low thermal expansion material.

3.2 Comparison with competitive materials

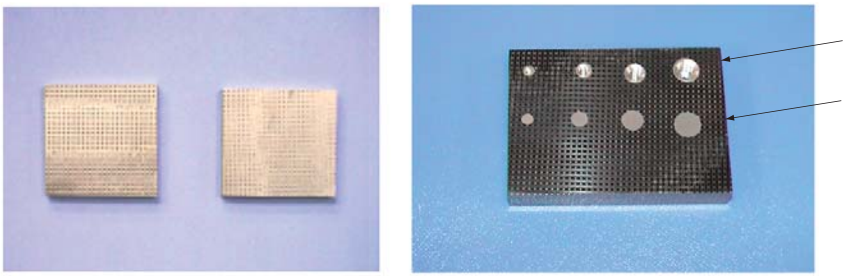
This developed material is superior to other competitive materials in that the coefficient of thermal expansion is very low and the specific strength and specific rigidity are extremely high. **Figure 9** shows a comparison of the coefficient of thermal expansion, and **Fig. 10** shows a comparison of the specific modulus of elasticity. **Table 1** shows a comparison of thermal and mechanical properties. The coefficient of thermal expansion of Invar is very small around room temperature. Above 100ºC, however, the Invar effect is lost, so Invar does not exhibit low thermal expansion characteristics and has the drawback of being magnetized.

Low thermal expansion glass has a very low coefficient of thermal expansion; however, it has a weakness in workability and the drawback of being incapable of forming a large object. With the material developed in

Table 1 Comparison of mechanical and thermal properties

Item	Unit	Extremely low thermal expansion	3DC/C	Invar	Super Invar	Zerodure
Density	g/cm^3	2.0	1.95	8.2	8.2	2.5
Modulus of elasticity	GPa	144	60	144	140	90
Specific modulus of elasticity	$GPa/(g/cm^3)$	72.0	30.8	17.6	17.1	36.0
Coefficient of thermal expansion	ppm K^{-1}	0.37	–0.7	1.2	0.13	0.02
Workability	–	Good	Good	Good	Good	Difficult
Large size	–	Possible	Possible	Possible	Possible	Impossible

(a) Plated test piece (b) Threaded test piece



(Note) Electroless nickel plating on the surface to a thickness of 5 μm (left) and 10 μm (right)

(Note) Drilled and cast and then threaded (M2, M4, M6 and M8, starting from the left)

Fig. 11 View of 3DC/C + Al composites

this study, blocks of up to about 450 mm cubes have been successfully made in the laboratory, and a larger size is possible.

3.3 Prospective uses

As a prospective use of this developed material, application to a wide range of fields is thinkable because of its extremely low thermal expansion characteristics. Its use is expected in parts for semiconductor exposure equipment, optics (laser equipment), base materials and die materials and also in the mirrors of a telescope.

If manufacturing technology is successfully established for a raw material having zero coefficient of thermal expansion, further expansion of use can be expected. **Figure 11** shows the appearance of an extremely low thermal expansion material made in our laboratory.

4. Future tasks

For practical application, machinability evaluation, a characteristic map of materials having various thermal expansion characteristics and an assortment are required. A cost reduction is an essential task and prerequisite for C/C composites.

In the future, we plan to address ourselves to this task based on the results introduced in this article and proceed with further research and development for practical application.

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