

A New Low Thermal Conductivity high temperature vacuum insulation composites with SiC Foam Core

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Abstract. With regards to the adiabatic principle for insulation, a new high-temperature vacuum insulation composites (HT-VIC) is put forward, which can be used in high temperature environment. Carbon fiber reinforced carbon composites have excellent high temperature resistance, high toughness, corrosion resistance and good thermal stability, etc. SiO₂ can be used to fill the microcrack and protect the carbon matrix from oxidizing. For this material, it is consisted of core material which is SiC foam ceramic and the flawless outer shell layer of carbon fiber reinforced composites by the methods of CVI (Chemical Vapor Infiltration) and silica sol vacuum impregnation, in the meantime the inside is a vacuum state. So the new ultra-temperature vacuum insulation composites with novel structure not only can be used at high temperature, but also has a very low coefficient of thermal conductivity compared with C/C and C/SiC composites. Material density is 0.81g/cm³, the effective thermal conductivity of UT-VIC ranged from 0.193 W/mK to 0.721 W/mK in 303K to 724K temperature, and the compression strength is 1.5 MPa. The aim of this paper is to investigate and analyze the effect of material structures and presents a possible future high temperature resistance vacuum insulation material.

Keywords: Vacuum insulation; SiC foam; Thermal conductivity.

I. Introduction

Thermal protection system (TPS) is one of the key technologies for developing Reusable launch vehicle (RLV) [1,2]. During the last several decades developments in heat transfer and use of thermal insulations in emerging technologies have extended the range of applications from cryogenic temperatures to high temperatures under reentry conditions into planetary atmospheres [3]. Traditional metallic thermal protection system was consisted of a metallic shell panel, fabricated from high temperature alloy and a fibrous insulation of light weight ceramic material [4]. While the metallic shell panel is easy to be softening and deformation at high temperature. So considering the limitation of metallic shell, the metallic thermal protection system maximum service temperature can't excess 1000°C. Investigations of thermo-physical properties of ceramic and refractory materials are important in

various fields of science, industry, and engineering [5-7].

Generally, high temperature insulation materials are multihole materials, considering their net structure [8-11]. And the conventional insulation materials considered for high temperature can be subdivided into three groups: fibers, microporous materials, and refractories (or fire clays), which is shown in Fig.1. Fibrous materials combine a low density of about 100 kg/m³ with a moderate thermal conductivity of 0.10 W/mK (20°C) to 0.35 W/mK (1000°C), respectively. Microporous materials available are of moderate density of less than 300 kg/m³ together with a low thermal conductivity of 0.02 W/mK (20°C) to 0.04 W/mK (1000°C), respectively, whereas fire clays are both of high density (more than 500 kg/m³) and have high thermal conductivity of up to 0.5 W/mK at 1000°C [12, 13]. Note that the fibers and microporous materials have very low thermal conductivity.

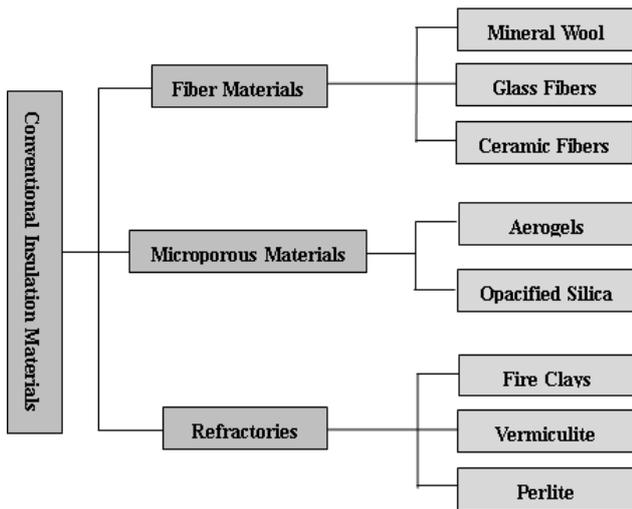


Figure 1. Conventional insulation materials classification

In this paper, the aim was to put forward a new high-temperature vacuum insulation composites (HT-VIC) which our group had reported before [14,15]. This composites design was used experience of adiabatic structure and the principle of vacuum insulation panel (VIP) for reference [16]. Figure 2 shown the physical diagram and schematic diagram of HT-VIC section. With regarding to the adiabatic principle for insulation, the inside of this composite was vacuum state which can be responsible for the reduction of the gaseous convection and conduction. Open cell SiC ceramic foam can be used as effective thermal insulation for high-temperature applications, which consists of a highly porous solid material. On the outside, carbon fiber reinforced ceramic matrix composites was used as a sealing layer, which had good thermal stability, oxidation resistance and excellent ablation resistance. This new composites with lighter and lower thermal conductivity have advanced innovation in high temperature insulation field and will have a great potential to substitute for conventional ceramic tiles to protect heat vulnerable regions of a launch vehicle such a space shuttle.

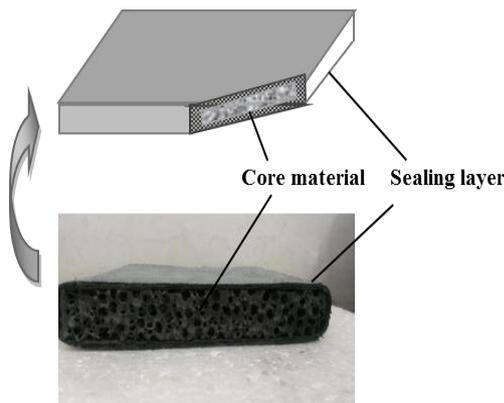


Figure 2. Physical diagram and schematic diagram of HT-VIC section

II. Experimental details

Raw materials, including core materials and carbon fiber sheet (CFS) (prepared in Changsha, PR China) were used in this study. SiC-matrix foam ceramics used as core materials with dimensions of 150 mm×150 mm×22 mm were provided by Suzhou DeXin Advanced Ceramics Co., LTD (Suzhou, PR China) , which the porosity was 85%. Figure 3 has described the main manufacturing steps of HT-VIC. In the first step, In order to prevent the PyC permeating the core material, 0.03 mm thick carbon paper was used as blocked layer attaching to the innermost carbon fiber sheet. Then the core materials were wrapped by 3-5 multilayer CFS. Third step, the setting agent was used to fix each sheet to avoid the gaps between layers. Fourth and final step further contained two processes. (I) Deposition of PyC at initial carbonfiber sheet by Chemical Vapor Infiltration (CVI) for 400 h to get a relatively dense sealing layer. (II) Densification, sealing and vacuum creation at the same time. The composites were manufactured by silica-sol infiltration sintering (SIS) method that included vacuum infiltration and vacuum sintering processes in an vacuum oven (10^{-1} Pa) at 450°C for 2 h. The whole processes were repeated 15 times to enhance the density of the composites.

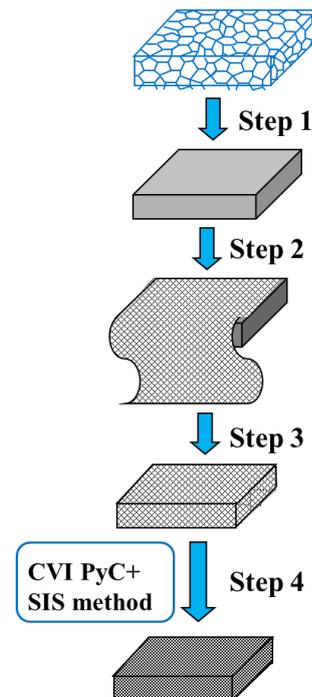


Figure 3. Detailed manufacturing steps of HT-VIC.

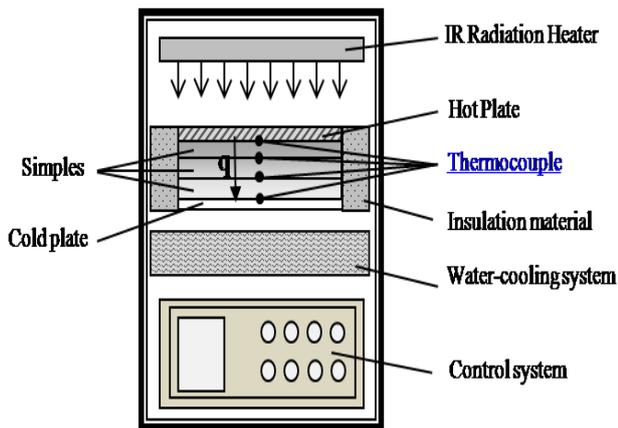


Figure 4. Schematic diagram of the water flow plate method apparatus.

After deposition, Effective thermal conductivity measurement was used water flow plate method, according to ASTM E422-05 standard [17]. As shown in Figure 4, the apparatus was heated up to the test temperature in accordance with the rules. After reaching the steady state, measuring sample hot and cold surface temperature, water flow and the water temperature difference can calculate the effective thermal conductivity of material according to the following formula.

$$\lambda = Q \cdot \delta / (A \cdot \Delta T) \quad (1)$$

Where λ is the effective thermal conductivity of material ($W/(m \cdot K)$), Q is heat of water absorption per unit time (W), δ is the sample thickness (m), A is the sample area (m^2), ΔT is the hot and cold surface temperature difference. The heat of water absorption is proportional to the specific heat of water, water flow and water temperature rise.

$$Q = C \cdot m \cdot \Delta t \quad (2)$$

Where C is the specific heat of water ($J/(g \cdot K)$), m is the water flow (g/s), Δt is water temperature rise (K).

III. Results and discussion

A. Microstructure characteristics of the composites

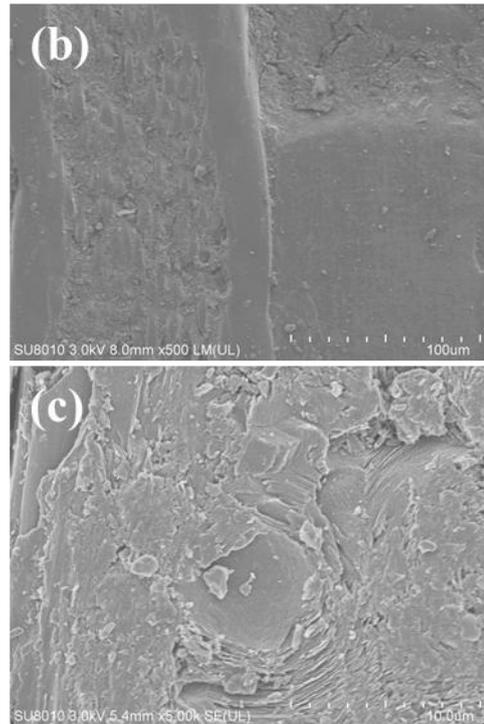
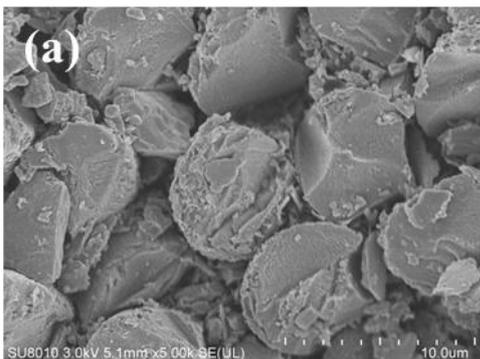


Figure 5. Microstructure of composites in different processing period: (a) before infiltrated with silica-sol; (b) after infiltrated with silica-sol; (c) the microstructure of sealing layer under higher magnification.

The pore morphology, size, distribution and content have significant effects on the thermal properties and heat conduct behavior. The shape of the pores is dominated by the fiber architecture at the inter yarn levels. Within each yarn, the progressive coating of the fibers creates longitudinal pores extending along the fibers. In low pressure chemical vapor infiltration (LPCVI) process, the infiltration of the pores is mainly dependent on the diffusion of the gaseous reactant. The C/C layer composites samples are mainly combine of two basic pores types: inter-fiber pores, between fibers in a bundle; inter-bundle pores, between fiber bundles in a fabric layer. In the LPCVI process, the smaller inter-fiber pore scan be easily filled by silicon carbide (CVI-PyC), but the larger inter-bundle is difficult to be completely densified because of both the slow deposition and the surface crust. Figure 5(a) shows the microstructure of C/C composites before infiltrated with silica-sol. From this micrograph, it is easy to find out that only the inter-fiber pores, between fibers in a bundle, within the CVI composites is infiltrated with CVI PyC. However, the inter-bundle pores between fiber bundles in a fabric layer are still remained. Figure 4 (b) shows the microstructure of composites after infiltrated with silica-sol. The micropores has been filled by silica. And it was more denser than that without impregnating silicasol. Figure 5 (c) shows the microstructure of sealing layer under higher magnification. From the Figure 5 (c), it is easy to

find out that both the inter-fiber pores and inter-bundle pores within the composites are infiltrated with sintered SiO₂. Thus, the sealing layer is densified by CVI and SIS methods completely.

B. Compressive loading

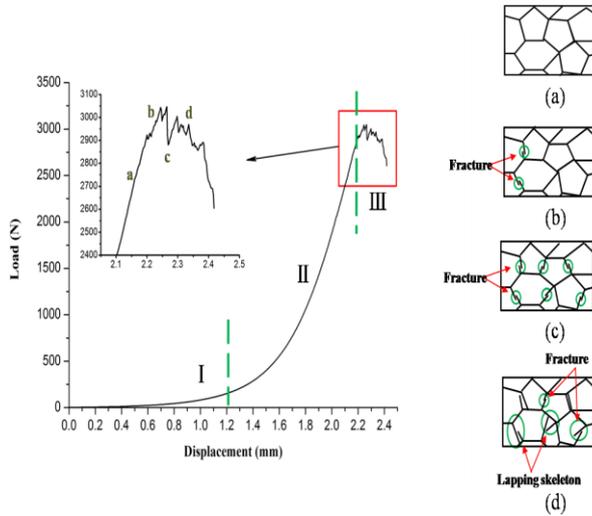


Figure 6. Compressive loading-displacement curve

Figure 6 shows the compressive loading-displacement curve of samples, while the SiC core materials play the main role to compressive strength of samples that is determined by the porosity and thickness of SiC skeleton. The average value of compressive strength of the samples was 7.5 MPa at room temperature. The load-displacement curve (see Figure 6) could be divided into three stages. At I stage, there was tiny load. Due to the initial load worked on the outer layer and the certain gaps had existed between the outer and core material. As the increase of displacement, gap disappeared gradually, then the load increased fast. At II stage, the mechanical behavior of the samples was nonlinear elastic. As the increase of load, the initial microcracks grow and expand in the SiC skeleton (Figure 6a). When the microcracks reach the surface of skeleton, fracture occurs. At III stage, the load presented a zigzag curve. It meant the SiC skeleton started to fracture with the increase in displacement. In aero b, a few of skeleton had fractured, while the other were intact (seen in Figure 6b), so the load could continue to increase. In aero c, the material showed a distinct and sudden stress drops with the increase in displacement. In this case, the most SiC skeleton underwent significant fracturing, it can be seen in Figure 6c. In aero d, with the displacement increase, fractured skeleton lapped joint together, as shown in Figure 6d, which led to the load increase again. However, with the displacement increased further, SiC skeleton fractured completely, the load decreased finally.

C. Effective thermal conductivity analysis

For the porous material, the heat transfer is mainly composed of gas heat convection λ_c and heat conduction λ_g , solid skeleton heat conduction λ_s as well as the thermal radiation λ_r of four parts, which can be exhibited by the expression [18,19].

$$\lambda_e = \lambda_c + \lambda_g + \lambda_s + \lambda_r \quad (3)$$

Figure 7 illustrates representative results of measurements with the ordinate showing the effective thermal conductivity in [W/mK] for UT-VIC, compared to SiC ceramic foam. The abscissa is the temperatures T_R in [K]. It could be seen both of them increased with the temperature, especially when the temperature was above 373K, the curve of effective thermal conductivity slope was greater. It was because the radiation became the dominant mode of heat transfer in the high temperature [9], when the temperature was below 373K, solid SiC skeleton heat conduction played the main role. Actually, the radiation contribution to the thermal conductivity in porous materials is a relation of the radiation temperature T_R to the third power which can be estimated by the expression [20]

$$\lambda_r = 4\sigma_B \epsilon n^2 d T_R^3, \quad (4)$$

In which σ_B is the Stefan-Boltzmann constant, ϵ the emissivity, n the refraction index and d is the pore diameter.

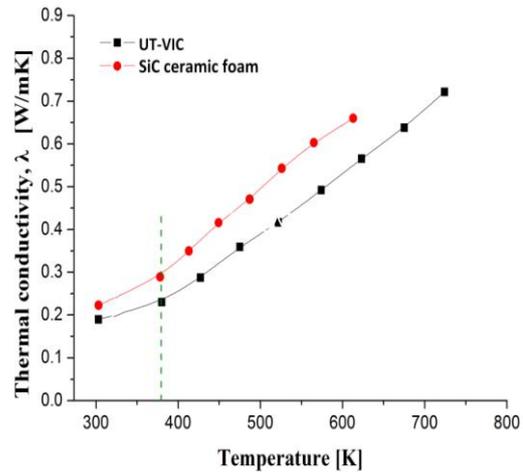


Figure 7. Temperature dependence of the effective thermal conductivity of UT-VIC, compared to SiC ceramic foam

Considering the thermal conductivity measurement in a static environment, gas diffusion velocity in pores is zero, Reynolds number R_e is below 22, which can clearly ignored the effect of gas heat convection λ_c on the effective thermal conductivity [21]. The gas conductivity λ_g is related to the conductivity at ambient pressure (λ_0) in the bulk and the Knudsen number which is defined by

the expression $K_n = lm/d$ where lm is the mean free path of the gas and d is the pore diameter by [13]:

$$\lambda_g = \frac{\lambda_0}{1 + 2\beta K_n} \quad (5)$$

Where β is a coefficient equal to 1.5 for air. λ_0 is a function of temperature. According to Handbook of Chemistry Physical Properties (2002) [22], at atmospheric pressure, the coefficient of thermal conductivity of dry air (λ_0) from 273 to 1373K has been given. Since there is no exact formula to calculate λ_0 , all these thermal conductivity datum of dry air were well fitted by MATLAB software to be a nonlinear expression of temperature (T):

$$\lambda_0(T) = a T^b \quad (6)$$

Where a about 3.93559×10^{-4} , b about 0.74588, T is in degrees Kelvin. In the experiments shown in Figure 7, the effective thermal conductivity of UT-VIC ranged from 0.193W/mK to 0.721W/mK in 303K to 724K temperature, compared to that of SiC ceramic foam ranged from 0.223W/mK to 0.664W/mK in 303K to 613K, which is 13.5-23.3% lower than that of SiC ceramic foam core materials. It should be emphasized the internal vacuum in composite, gas heat convection and heat conduction are not existed, result in some decline of effective thermal conductivity. However, owing to the intrinsic high thermal conductivity of SiC material (42.5W/mK at 400K for 21.7% porosity) [22], the heat was mainly passed through the SiC foam skeleton, coupled with thermal bridge effect of sealing layer, leading to the thermal conductivity of composites decreased unobviously after vacuum inside. Based on this, the relationship between vacuum degree and solid skeleton heat conduction will be researched in the next step.

IV. Conclusion

In this work, new ultra-temperature vacuum insulation composites with vacuum inside were successfully fabricated by CVI PyC+silicasol-infiltration-sintering method. The effective thermal conductivity of SiC ceramic foam and UT-VIC were investigated experimentally. First, both of them increased with the temperature due to the radiation mechanism. Considering vacuum inside, gas heat convection and heat conduction were not existed, the effective thermal conductivity of UT-VIC ranged from 0.193W/mK to 0.721W/mK in 303K to 724K temperature, compared to that of SiC ceramic foam ranged from 0.223W/mK to 0.664W/mK in 303K to 613K, which is 13.5-23.3% lower than that of SiC ceramic foam core materials.

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VI. References

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