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Novel designs of charring composites based on pore structure control and evaluation of their thermal protection performance

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ABSTRACT

To improve the thermal protection performance of the charring composites in reentry vehicles subjected to the challenged aerothemodynamic environment, we design six kinds of charring ablators based on the pore structure control. At the same time, a thermal-fluid-chemical coupled ablation model is developed for evaluating the designed ablators' performances. Based on this model, the coupled thermal-fluid-chemical responses of an existing composite with homogeneous pores' distribution are calculated to validate the developed model. After that, the numerical results of the pore structure controlled charring composites indicate that a charring ablator with a reasonable pores' distribution will have better thermal protection performance, especially in which the initial pores' content rise at the locations near the ablator's bondline and in the middle of the thickness. This study will be a guidance for the design of charring composites for thermal protection application in reentry vehicles in a quantitative and efficient manner.

1. Introduction

The charring composites normally provide the most efficient thermal protection shield for the thermal protection system (TPS) of the hypersonic reentry vehicles, due to their low thermal conductivities and low densities, the ability to absorb heat through the pyrolysis of resin matrix, and rejecting heat via pyrolysis gases injection back into the boundary layer gas [1,2]. Improving the performances of charring ablators is a necessary and critical issue in recent years, such as reducing their thermal conductivities and cutting down their weight to enhance their ability for the challenged aerothermodynamic environment [3,4].

Beginning from the 50s of last century, with the manufacture of the Mercury, the Apollo, the Gemini and the Soyuz spacecrafts, the densities of the charring ablators used in their TPS varied from high values to low ones, which were represented by the CMCP composites and the AVCOAT-5026-39H/CG for the Apollo [5,6]. From the end of the 1960s to the beginning of 70s, the TPS material of American Mars probe craft, the Viking, was composed of the heat insulation tiles using a low density charring ablator named SLA [7]. In the 1990s, the charring material impregnated by the silicone resin named SIRCA with the density range from 0.18 g/cm^3 to 1.00 g/cm^3 was successfully developed by NASA's Ames Research Center, and it was used in the TPS of the Mars Pathfinder and the Mars Exploration Rover. The phenolic impregnated carbon ablator (PICA) was focused by the researchers since the 1990s. It has already been used as the thermal protection layer of the Stardust spacecraft. And there were reports in 2010 and 2012 by NASA that PICA would be adopted as the thermal protection tiles for the Mars Science Laboratory and the Dragon crafts [8–10]. However, the traditional charring ablators introduced above cannot well satisfied the challenged aerothermodynamic environment for today's spacecraft missions, which makes the vehicles under a longer reentry time, a oxidative environment, and a larger cold wall heat flux, since the traditional ones owning a poor antioxidation capacity, a low char residual rate after the pyrolysis of the resin, a lower strength and a little higher thermal conductivity. There were two major ways to improve the thermal protection performance of the charring ablators in recent years. One was adding a thermal protective clothing on the surface of the charring ablator [11–13]. But this clothing would be failed gradually with the increasing of the surface temperature especially when the vehicle was under a quite long reentry time. The other was increasing the porosity, decreasing the thermal conductivity, enhancing the strength etc. of the ablator by the material modification. The common methods for these material modification are summarized as follows: Firstly, the resin was modified by introducing inorganic elements, aromatic rings or aromatic heterocycles to etherification, esterification and heavy metal chelating of phenolic hydroxyl groups. But the char residual rates after ablation were not higher than 60%

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Nomenclature

L	thickness of ablator [m]	F	mass lost fraction [–]
x	spatial coordinate in axial direction [m]	ξ	advancement of pyrolysis reaction [–]
t	time [s]	χ	molar fraction [–]
ρ	density [kg/m^3]	y	mass fraction [–]
c_p	specific heat [J·kg^{-1}·K^{-1}]	A-D	coefficients in empirical equation [–]
k	thermal conductivity [W·m^{-1}·K^{-1}]	a_1-a_6	coefficients in empirical equation [–]
ε	porosity [–]	Ψ	diffusion flux [kg·m^{-2}·s^{-1}]
κ	permeability [m^2]	D_k	diffusion coefficient [m^2/s]
μ	viscosity [Pa·s]	Le	Lewis Number [–]
h	enthalpy [J/kg]	ι	tortuosity [–]
Δh_p	pyrolysis heat [J/kg]	α	absorptivity [–]
M	molecular weight [kg/mol]	η	emissivity [–]
E	activation energy [J/kg]	σ	Stefan-Boltzmann constant [W·m^{-2}·K^{-4}]
A	exponential factor [1/s]		
n	order of reaction [–]	*Subscripts*	
p	pressure [Pa]	v	virgin
T	temperature [K]	c	char
v	velocity [m/s]	g	gas phase
c	residual rate [–]	s	solid phase
Π	pyrolysis gas production rate [kg·m^{-3}·s^{-1}]	i	species index
π	species production rate [mol·m^{-3}·s^{-1}]	j	reaction index

by this method [14,15]. Secondly, the novel resin system was developed, such as the polybenzimidazole, the polyquinoline, the polybenzoxazole, the polybenzothiazole and the polyimide resin. But there were still problems in the molding process, the price and the raw material supply in this method. Lastly, by adding fillers to the resin to control the pore structure like the pores' distribution and size in the ablator, the char residual rate after the pyrolysis reactions of the resin could be increased and the ablator's thermal conductivity could be decreased, then the strength of the char material and the heat insulation performance of the ablator could be promoted [16]. For example, Pelin et al. incorporated nanometric silicon carbide into phenolic resin and found the addition having positive effect on the mechanical, the thermo-mechanical and the tribological performance [17]. Botelho et al. focused on the viscoelastic evaluation of phenolic resin reinforced carbon nanotubes (CNTs) and reported that the viscoelastic properties and the thermal stability could be significantly enhanced and modified by a relative small amount of CNTs in a phenolic resin matrix [18]. Park et al. evaluated the mechanical and the thermal properties of graphite oxide (GO)-phenolic composites with different sizes of GO and showed them exhibited better thermal stability in both thermal analysis and flame retardant testing [19]. Wang et al. prepared a modified phenolic resin using thermal prepolymerization between barium-phenolic resin and modifier. The test of the novel resin showed that there were some carbon structures with the nanopores in a range of between 30 nm and 150 nm and the thermal conductivity of modified phenolic resin could be reduced by nearly 50% [20].

In conclusion, more and more researchers start to focus on the design of the charring ablators of today's hypersonic reentry vehicles yielding to the severe challenged aerothermodynamic environment by improving the ablators' performance by material modification. Unfortunately, these methods have just modified the resin matrix by random approaches, such as adding fillers disorderly into the matrix. Although most of the researches proposed that the novel modified composites own low thermal conductivities due to their small pore diameters and high porosity, they still could not give a qualitative guidance to design novel charring composites, for example, in which the different value of the porosity of the ablator in different range in the thickness direction should be given directly. Also, simulation is a speedy and efficient way to evaluate the thermal protection performance of different designed ablators. So it is urgent to develop an ablation model for the pore structure controlled charring ablator to help finding out the design scheme with the best thermal protection performance, which must take the variation of pores' distribution into consideration and is significant different with the pyrolysis layer ablation model in our previous researches [21–24] and other heat transfer models for the ultrahigh-temperature composites [25–27]. The novel designs of charring composites to improve their thermal protection performance remains longstanding challenge. Toward this objective, in this manuscript, we will design six kinds of pore structure controlled charring ablators to explore whether the variation of pores' distribution can improve the thermal protection performances of the charring composites. And we will develop a thermal-fluid-chemical coupled ablation model for the pore structure controlled charring ablator on the basis of the mass, the momentum, and the energy conservations and validate this model using a non-designed existing charring ablator with a constant porosity. Furthermore, the coupled thermal-fluid-chemical responses of the designs and the non-designed ablator are calculated and compared using this model. Finally, the best design scheme will be given by analyzing the thermal protection performance of all the ablators.

2. Model

2.1. Physical model

According to the ablation mechanisms of the charring composites, as the ablator undergoes heating due to incident heat flux, the heat transfers from the material's surface to its bondline. Meanwhile, the resin matrix undergoes pyrolysis and absorbs heat with pores formation, in which the produced pyrolysis gases flow and inject out of the surface. The main heat starts to be absorbed through the endothermic pyrolysis of the matrix which is called the body-ablation process. If the antioxidants are added into the charring material during manufacture of material or the environmental gases are inert, there is no recession on the outer surface.