Stress and damage development in the carbonization process of manufacturing carbon/carbon composites

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ABSTRACT

Carbon/carbon composites are widely used in aerospace industry due to their excellent mechanical and thermal properties in high temperature. However, understanding of the mechanism for defects induced in the carbonization process of carbon/carbon composites is still inadequate. In this paper, a model is established to obtain the matrix properties and simulate the stress and damage evolution during the carbonization process of carbon/carbon composites. First, the phase evolution equations are used to gain the volume fractions of phases, and then the elastic modulus and Poisson ratio are obtained by a nested homogenization method. Then, the thermal deformation including the competition between thermal expansion and chemical shrinkage is discussed. The damage evolution in the matrix is incorporated through the progressive damage model. Finally, we perform the finite element simulation for the carbonization of the unidirectional fiber bundle reinforced carbon/carbon composites. The results show that matrix sustains compression circumferential stress before reaction start. After reaction activates, the circumferential stress turns to tension due to the matrix shrinkage, and the tension stress increases rapidly to cause damage. The damage evolves along the fiber/matrix interface with the temperature increasing. With damage accumulation, micro cracks may generate along the fiber/matrix interface, which is similar as the literature reported.

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1. Introduction

Carbon/carbon composites possess many excellent properties over other conventional materials, such as high ratio of mechanical properties versus density at high temperature, low thermal expansion, and high thermal and chemical stability [1–3]. As an attractive material in aerospace field, the demands for this material have increased tremendously recently. In order to obtain satisfactory products, a fundamental understanding of the manufacture process is essential for quality control and product optimization.

The preparation of carbon/carbon composite materials can be roughly divided into three steps: The resin is firstly impregnated into the carbon fiber architectures. After that, the composite is put into the furnace for carbonization in a flow of nitrogen. Finally, the densification process is adopted until reaching the desired density. In the carbonization process, the pyrolysis reactions convert the resin matrix to amorphous carbon phase and gas phase. Gaseous products are released and a highly porous carbon/carbon preform are left. The actual process of thermodecomposition in the manufacture of carbon/carbon composites materials is very com-

plex, which involves many coupled mechanisms, both mechanically and chemically. Various events such as phases tranformation, internal stress and strain generation, internal damage and defects, and matrix degradation exist simultaneously at the same process, and they have large effects on each other. The detailed physical and mechanical essence are still not clearly described.

A large number of researches have been carried out on the carbonization process of carbon/carbon composites. However, most of these researches foucs on the chemical reaction kinetics [4–6]. Only a few studies concern about the evolutions of stress and damage during the carbonization. Dimitrienko [7–11] proposed a porous materials model to obtain the volume fraction of resin, carbon and gas during the carbonization process and then the effective mechanical properties, thermal deformation considering the chemical shrinkage and stress characteristics were discussed. Schulte-Fischedick [12–15] identified different crack types that occured during carbonization process using thermo-microscopy and acoustic emission analysis. They noted that the creation of cracks were driven by the high shrinkage of matrix. Kim [16–19] established a model for stress and displacement predictions using two-dimensional finite element method. In his model, the composites properties were gained by the micro-mechanical model pro-

posed by Bogetti [20] and the mechanical property degradation was simulated based on the crack density from the experiment. Besides, Rajneesh Sharma [21–23] found that there exsited voids and cracks in manufactured carbon/carbon composites which were induced during manufacturing process, and they furtherly proved that the internal defects had a larger effect of on the mechanical properties of carbon/carbon composite materials.

So far, the mechanism of the internal stress generation and the formation of local defects are still not accurately described. The competition between thermal deformation and chemical shrinkage and its effects on the internal stress still need to be discussed. The aim of this paper is to investigate the mechanism for internal stress generation and damage developments during the carbonization process by numerical methods. First of all, a basic model to describe the evolution of volumetric fraction for different phases is introduced. And then, the thermal deformation behaviors including the competition between thermal expansion and chemical shrinkage are discussed, which will be taken into the final meso-mechanical finite element (FE) model. A progressive damage model is also adopted into the FE model for simulating the internal damage evolution in matrix. Finally, a FE analysis on a representative unit cell for unidirectional fiber bundle reinforced carbon/carbon composites is performed to study the internal stress generation, the internal damage formation and evolution during carbonization process.

2. Related equations in the carbonization process

2.1. The phase evolution equations and the effective elastic properties

During the carbonization process, the resin matrix is transformed into pyrolytic carbon and gas. Therefore, chemical compositions of the composite changes with the temperature. Besides the reinforcing fiber, there are four phases in the matrix: solid resin, liquid resin, pyrolytic carbon and gas. Because the liquid resin only exists in the initial stage of carbonization and its amount is pretty small comparing to solid resin, it is ignored in the next phase evolution equations. And since most generated gas is released, the gas phase is replaced by void phase in the subsequent discussion. When the pyrolysis of the matrix happens, the volume fraction of the three phases vary and satisfy the following relationship: $\phi_r + \phi_c + \phi_v = 1$, where ϕ_r, ϕ_c and ϕ_v are the volume fraction of resin phase, pyrolytic carbon phase and voids phase, respectively. Eventually, the volume fraction evolution equations of each phase in the carbonization process are described as follows, which are based on heat-mass transfer relationship [7].

$$\begin{cases} \rho_r \frac{\partial \phi_r}{\partial t} = -J_r \\ \rho_c \frac{\partial \phi_c}{\partial t} = (1 - \Gamma_r) J_r \end{cases} \tag{1}$$

where ρ_r, ρ_c are densities of solid resin phase and pyrolytic carbon phase, respectively. Γ_r is the gasification coefficient concerning to the phase transformation. The rate of the pyrolysis reaction J_r is described by the equation in the Arrhenius type:

$$J_r = J_r^0 \phi_r \exp\left(-\frac{Ea_r}{RT}\right) \tag{2}$$

here T is current temperature, J_r^0 and Ea_r are pre-exponential factor and activation energy of the thermal pyrolysis reaction of the matrix. Based on above equations, the phase fraction evolution in the composite can be determined with the temperature variation of the system.

Due to transformations of compositions, the material properties of matrix are changing in the carbonization process. As the composites are made of three different phases at the same time, a nested homogenization method based on the Mori-Tanaka model is used to estimate the effective elastic properties. In the first step, the solid resin as a matrix is homogenized with the pyrolytic carbon as the inclusion. And then the effective material whose properties are obtained above acts as a fictitious matrix reinforced with voids as another inclusion to constitute the real material. The trial computation shows that the sequence of the inclusion has few influence on the final results.

2.2. The thermal deformation behaviors of matrix

In conventional fiber reinforced polymer matrix composites, one important reason for the residual stresses/strains generation is the mismatch in the coefficient of thermal expansion (CTE) of the fiber and matrix. As for carbon/carbon composites during carbonization process, things get more complicated. The thermal deformation of matrix is not just depended on the thermal expansion. The chemical shrinkage induced by the pyrolysis reaction would also change the volume of matrix. With the phase transformation, the competition between thermal expansion and chemical shrinkage will change, and thus affect the thermal deformation of matrix.

Thus, during the carbonization process, the thermal deformation of matrix identified by the thermal strain ε_m, can be divided into three parts: the thermal expansion of resin matrix, the thermal expansion of carbon matrix and the chemical shrinkage due to reaction. It can be expressed as [7]:

$$\varepsilon_m = \alpha_r \phi_r (T - T_0) + \alpha_c \int_0^t \dot{\phi}_c (T(t) - T(\tau)) d\tau - \beta_c \phi_c \tag{3}$$

here α_r and α_c are the thermal expansion coefficients of resin matrix and carbon matrix, respectively. β_c is the chemical shrinkage coefficient. T_0 is the reference temperature.

Finally, the apparent thermal expansion coefficient α_{eff} during the carbonization process can be defined as:

$$\alpha_{eff} = \varepsilon_m / (T - T_0) \tag{4}$$

When α_{eff} is positive, it means the matrix expand with temperature increasing. Otherwise, the matrix shrinkage happens.

2.3. Evolution of damage

A progressive damage model is introduced to simulate the initialization and evolution of damage in matrix during carbonization process. The material behavior is assumed to be isotropic. When the maximum principal strain ε_{max} exceeds the failure strain ε_d, the material begins to be damaged and the damage factor evolves according to the equation as follow:

$$d = 1 - \frac{\varepsilon_d}{\varepsilon_{max}} \exp\left(-\frac{C_0 \varepsilon_d (\varepsilon_{max} - \varepsilon_d) L_c}{G_m}\right) \tag{5}$$

where C_0 is the initial stiffness of the matrix without any damage, and L_c is the characteristic length associated with the elements geometry, which does help to minimize the mesh sensitivity in the numerical simulation [24]. G_m is a parameter which control the failure progresses.

The initiation and evolution of the damage would induce the materials degradation. Thus, the local effective elastic properties is updated once the damage increases, and then the local stress status need to be re-calculated to check whether new damage happens before next iteration.

3. Numerical model

The meso-mechanical model is set up based on the representative volume element (RVE) technique. A 2D unit cell of a unidirec-