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Improved ablation resistance of carbon–phenolic composites by introducing zirconium silicide particles

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ABSTRACT

The effect of $ZrSi_2$ on the thermal degradation behavior of phenolic and the role of $ZrSi_2$ on the ablation resistance of carbon–phenolic (C–Ph) composites are investigated by introducing $ZrSi_2$ particles into phenolic, and then $ZrSi_2$ particles into C–Ph composites. Thermogravimetry (TG) analysis illustrates that the residue yield of phenolic at high temperatures is increased by the introduction of $ZrSi_2$ particles. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses reveal that the increased residue yield is attributed to the reactions between $ZrSi_2$ particles and pyrolysis volatiles. Therefore, partial carbon and oxygen elements in the volatiles remain in the thermal residue in the forms of amorphous carbon, ZrO_2 and SiO_2, respectively. Moreover, the ablation resistance of C–Ph composites is significantly improved by the introduction of $ZrSi_2$ particles with formation ZrO_2 and SiO_2 during the oxygen–acetylene ablation process. The average linear and mass ablation rates of $ZrSi_2$ modified carbon–phenolic (Z/C–Ph) composites evidently reduce by comparison with those of C–Ph composites under similar conditions. As depicted in the microstructure, the ablation occurs in volume in C–Ph composites. The oxygen-containing molecules penetrate deeply inside the matrix, thus the ablation by oxidation is accelerated. However, the ablation occurs in surface in Z/C–Ph composites. $ZrSi_2$ reacts with the oxygen-containing molecules to form SiO_2–ZrO_2 layer and molten SiO_2 cover on the ablated surface, thus the ablation by the oxidation of matrix and fibers in the interior has been inhibited.

1. Introduction

Ablative materials are critical for thermal protection system (TPS) in space applications, protecting space vehicle against the aerodynamic heating encountered in hypersonic flight [1]. Carbon-fiber-reinforced composite materials have been known to be useful for the purpose of high-temperature ablation resistance [2–10]. Specially, in moderate ablation environments, the carbon–phenolic (C–Ph) composites are considered extensively to be efficient ablative thermal protection materials [3,9–14]. When the C–Ph composites are subjected to ablative conditions in air, it would be most desirable if the fiber reinforcement and matrix retain their own structure, property and shape to as great an extent and far as long as possible. Therefore, there is always an urge to improve the ablation resistance of C–Ph composites.

Recently, different kinds of nanoparticles, such as nanosilica and carbon nanotubes (CNTs), have been studied to improve the ablation resistance of C–Ph composites. I Srikanth et al. [15] manufactured the high ablation resistance rayon-based carbon–fabric/phenolic composites using nanosilica powder as a filler material. Nanosilica filled carbon–phenolic composite exhibited higher ablation resistance compared to the unfilled composite. The thermal degradation of phenolic resin was considerably restricted by the addition of silica [16]. Aidin Mirzapour et al. [17] studied the effect of nanosilica on the mechanical, thermal and ablation properties of chopped carbon fibre/phenolic composites. They observed better thermal stability and ablation response in nano-modified samples. Joung-Man Park et al. [18] evaluated the effects of carbon nanotubes and carbon fiber reinforcements on thermal conductivity and ablation properties of carbon/phenolic composites. Both carbon fiber mat and CNT/phenolic composites exhibited much better thermal conductivity and ablation properties than that of neat phenolic resin. Zuo-Jia Wang et al. [19] indicated that the uniformity of the CNT dispersion played an important role in the ablation resistance of CNT filled phenolic composites. Zahra Eslami et al. [20] investigated the thermal, mechanical and ablation properties of carbon fibre/phenolic composites filled with multi-wall carbon nanotubes (MWCNTs). The linear and mass ablation

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rates of the nanocomposites were distinctly decreased after modified with small amount of MWCNTs. A strong network char layer without any cracks or opening was formed, which was due to the presence of MWCNTs in the composite. Maurizio Natali et al. [21] conducted a comparative study on the ablative properties of carbon black and MWCNT/phenolic composites. The dimensional stability of composites was increased by the introduction of carbon black and MWCNTs.

Besides the introduction of nanoparticles, introducing zirconium diboride particles or unique structure materials into C–Ph composites has also attracted considerable attention due to the improved ablation resistance. Yaxi Chen et al. [22] introduced ZrB_2 particles into C–Ph composites and discussed the role of ZrB_2 on the ablation process. ZrB_2 could react with the oxygen-containing molecules on the surface during the ablation process. The ablation resistance and insulation performance of C–Ph composites could be notably improved by the formation of ZrO_2 and B_2O_3. Zahra Amirsardari et al. [23] used ZrB_2 and graphene oxide (GO) as reinforcements to control hot corrosion of carbon/phenolic composite during high-temperature ablation. The ablation rate could be significantly decreased by the presence of ZrB_2 with formation ZrO_2 grains in phenolic composite.

As we all known, ablation process is a thermochemomechanical phenomenon which involves complex chemical and physical reactions [24]. Since carbon fiber and carbonized phenolic are carbon material, they are susceptible to oxidation at high temperatures. In this study, from the point of view on inhibiting oxidation during the ablation process, zirconium silicide ($ZrSi_2$) particles have been introduced into C–Ph composites. As one of refractory silicides with low density, $ZrSi_2$ has high Young's modulus and compressive yield strength at high temperatures [25]. Moreover, $ZrSi_2$ has good oxidation resistance at high temperatures [26]. $ZrSi_2$ forms a surface layer of silica due to oxidation at elevated temperatures. The presence of silica can accelerate the densification and act as a protective barrier against high-temperature oxidation. These properties would allow $ZrSi_2$ to be considered as excellent candidates for high temperature applications. Wen-Cheng J et al. [27] have developed a multi-layer coating containing $ZrSi_2$ on C/C composites. The resistance to thermal ablation and cyclic oxidation of C/C composites were significantly improved by the formation of zircon, cristobalite, and zirconia in the oxidized layer of the coating.

To the best of our knowledge, few works have been conducted on the thermal stability, ablation performance and microstructure of C–Ph composites containing $ZrSi_2$ particles. The aims of this paper are: (i) to study the effect of $ZrSi_2$ on the thermal degradation behavior of phenolic, and to investigate the thermal residue constituents of $ZrSi_2$ modified phenolic (Z/Ph) composites after TG analysis; (ii) to manufacture $ZrSi_2$ modified carbon–phenolic (Z/C–Ph) composites, and to study the role of $ZrSi_2$ on the ablation resistance of C–Ph composites; (iii) to study the microstructure of the ablated specimens to understand the mechanisms operating during ablation.

2. Experimental

2.1. Materials

Resole-type phenolic resin (Shanxi Taihang fire resistant polymer Company) was used as matrix of composites. The content of free phenol was less than 7 wt%. Ethanol (Sinopharm Chemical Reagent Co.) was used as solvent and purity > 95%. Plain weave carbon fiber cloth (Wuxi Weppom Composite Materials Company) was used as reinforcement of composites. $ZrSi_2$ particles (Shanghai Aladdin Reagent Factory) were used as filler materials and had the particle size distribution of 1–5 μm and purity > 95%.

2.2. Sample preparation

2.2.1. Fabrication process of Z/Ph composites

Phenolic resin was ground into micro-sized powders by high-energy ball-milling technique. Then, the phenolic resin powders were mixed with $ZrSi_2$ particles in the mass proportion of 1:0.2 by mechanical mixing. The mixed powders were put into a beaker and cured at 140 °C for 2 h, followed by 175 °C for 2 h, and then 200 °C for 1 h, all in a vacuum oven at a vacuum pressure 0.090 MPa. Finally, the porous Z/Ph composites were detached from the beaker and ground into powders for thermogravimetry analysis. Neat phenolic resin was also fabricated into sub-sample with the same fabrication process.

2.2.2. Fabrication process of Z/C–Ph composites

Phenolic resin was diluted using ethanol by mechanical mixing. $ZrSi_2$ particles were added to the phenolic resin solution by mechanical stirring for 2 h, then the mixture was under ultrasonic treatment for 1 h, and uniform mixture solution was obtained. The mixture solution contained phenolic, ethanol and $ZrSi_2$ particles at the mass ration of 1:1:0.2. Plain weave carbon fiber cloth was impregnated with the above mixture for 30 min. Then the impregnated cloths were left in the prepregging rack at ambient temperature for 20 ~ 24 h to evaporate the solvent inside. Prepared prepegs were cut into 60 × 90 mm pieces, stacked up and fabricated in a vulcanizing machine by compression molding. The curing process is shown in Fig. 1. Finally, the Z/C–Ph cured composites (0.718 g/cm^3) were fabricated into cylindrical samples with sizes of Φ29.3 × 10 mm for the oxygen–acetylene ablation testing, and the C–Ph composites (0.694 g/cm^3) were also fabricated into sub-samples of Φ29.3 × 10 mm. This mixture contains ethanol and phenolic at the mass ration of 1:1.

2.3. Characterization and testing

The cured phenolic and the cured Z/Ph composites were subjected to thermogravimetry (TG) analysis in N_2 atmosphere at a constant heating rate of 5 °C/min from 40 °C to 1200 °C in a NETZSCH STA 449 F3 typed thermal analyzer. Experiments for each test were repeated three times in order to confirm the reproducibility of the results. The weight of the sample for each test was approximately 20 mg. The thermal residues of phenolic and Z/Ph composites after TG analysis were characterized by X-ray diffraction (XRD) analysis in a D8 Advance X-ray diffractometer. Each scan was conducted from a 2θ angle of 10 ~ 70° at a scan rate of 5°/min. One sample was tested for each scan. The thermal residue of Z/Ph composites after TG analysis was also characterized by X-ray photoelectron spectroscopy (XPS) in an AXIS ULTRADLD apparatus. One sample was tested for this characterization. Curve fitting of the band of Zr_{3d} or Si_{2p} was carried out assuming a Gaussian peak: the curve fitting was made by generating and combining Gaussian samples. The heights, horizontal positions, and half-value widths of these shapes were determined so that the combined shape was in agreement with the measured one. Ablation performances of C–Ph composites and Z/C–Ph composites were tested under oxygen–acetylene torch with a heat flux of 4.28 ± 10% MW/m^2 for 60 s. The flow rates of oxygen and acetylene were 1500 l/h and 1100 l/h, respectively. The oxygen–acetylene gun with 2 mm diameter was vertical to the surface of the sample, and the distance from gun to the surface of the sample was 10 mm. The linear ablation was performed at the sample center. The mass ablation rate was the average of the entire sample. Five-point average thickness and weight changes, obtained from the measurements taken before and after ablation, were used to calculate the average and standard deviation of the linear and mass erosion rates. Microstructure