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Fabrication and characterization of ZrW$_2$O$_8$-Cf/E51 negative thermal expansion composite

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Abstract

ZrW$_2$O$_8$-Cf/E51 composite with a negative Coefficient of Thermal Expansion (CTE) was fabricated by a method combining mechanical stirring with ultrasonic vibration, then microstructures and properties of the composites were analyzed and summarized by scanning electron microscope (SEM), DIL 402 C thermal expansion tester and electronic universal testing machine. The results showed that particles distribution defects and impregnation defects of carbon fibers would occur when the process parameters were not controlled properly. Long curing time and low viscosity could cause particle settling and accumulation. The experimental results confirmed that the CTE (about $-0.52 \times 10^{-6}/\text{°C}$) and tensile strength (about 440 MPa) of E51 resin were improved with the addition of carbon fibers and ZrW$_2$O$_8$ particles.

1. Introduction

Coefficient of Thermal Expansion (CTE) is an important parameter of thermal physical properties. In recent years, with the rapid development of high-tech materials, people not only require the materials with high performance and lightweight characteristics, but also require the materials with high dimensional stability to cope with the adverse effects of temperature changes in extreme environments [1, 2].

Researches show that most of the traditional structural materials have the inherent property of thermal expansion and contraction. Size change will occur when the ambient temperature changes, which will result in the loss of accuracy, failure of function and damage of engineering structure [3]. For example, the position accuracy between the primary mirror and the secondary mirror of the astronomical optical telescope will change due to the influence of thermal expansion and contraction. The thermal deformation of antenna support of communication satellite will lead to antenna offset and deviation from ground communication, and the huge temperature difference experienced by satellite in space will lead to incompatible thermal deformation and spalling of solar cell and substrate [4]. The development of materials with low/negative CTE, high strength and lightweight has become one of the frontier scientific and technological fields that scientists all over the world focus on [5, 6].

At present, traditional structural materials are no longer meeting the demands, and composites become the emphasis of researches in materials science due to their designable characteristic [7–9]. The commonly used methods to control thermal expansion behaviours of composites are the fiber arrangement control method and the negative expansion particles addition method. The main idea of the fiber arrangement control method is to utilize the negative thermal expansion characteristic of fibers in the axial direction [10–12]. Single-PLY fiber reinforced composites can achieve unidirectional zero or negative CTEs by the reasonable design of fiber arrangement. Furthermore, the in-plane zero or negative CTEs of the fibers reinforced composites with excellent mechanical properties can be obtained by arranging the different single-plies with unidirectional zero or negative CTEs [13]. Rangarajan et al [14] provided a proof that the smallest value of effective measure of the
CTE is rendered by straight fiber path configurations using the sum of the CTE values along the principal material directions. Praveen et al. [15] designed zero thermal expansion composites with carbon fibers and glass fibers, which can be used in a low temperature environment. Hassanzadeh et al. [16] established a micromechanical model of glass fibers reinforced composites containing nano-silica particles, and studied the effects of fiber volume fraction, aspect ratio and interlayer thickness on CTEs and mechanical properties of the composites. It is noteworthy that the method of optimizing fiber arrangement has not fundamentally solved the problem because the mismatch of CTEs of fibers and matrix often leads to interfacial damage or interlaminar cracking [17].

On the other hand, the main ideal of the negative expansion particles addition method is to adjust the CTEs of the composites by adding negative expansion particles. The composites with negative expansion ceramics, oxides and ferroelectric ferromagnetic materials as the reinforcements and metals (Al, Cu, Ti, etc), ceramics and polymer as the matrix have been reported in the literature. Since Sleight’s team [18] found zirconium tungstate ($\text{ZrW}_2\text{O}_8$, CTE is $-8.7 \times 10^{-6}/\text{°C}$) had negative CTEs in a wide temperature range, $\text{ZrW}_2\text{O}_8$ particles had attracted more and more attention as a kind of thermal expansion regulating phase [19–21]. Through the study of phase transformation decomposition, researchers have found that $\text{ZrW}_2\text{O}_8$ can be stable in service below $770 \text{ °C}$ and the decomposition temperature range is $780 \sim 1108 \text{ °C}$[22], which is an ideal negative expansion control phase. However, $\text{ZrW}_2\text{O}_8$ particles might lead to lower strength of composites.

Although there exists a great mount of studies on the composites with low/ negative CTEs, limited researches focus on the fabrication and characterization of $\text{ZrW}_2\text{O}_8$-C/G/E51 composites. By adding $\text{ZrW}_2\text{O}_8$ particles into carbon fiber reinforced composites, not only the CTEs of composites can be reduced, but also the difference of CTEs between the fibers and the matrix resin can be reduced, because the CTEs of the composites depend on the CTEs of both the fibers and the matrix [5, 23].

The main objective of this study is to analyse the generation mechanism of fabrication defects of $\text{ZrW}_2\text{O}_8$-C/E51 composites with negative CTEs. Based on the microscopic observation, the causes of defects in the process of particle dispersion and resin infiltration are analysed, and the reasonable process parameters for the successful preparation of composites are discussed. Finally, the CTEs and mechanical properties of the composites are experimentally tested.

2. Materials and methods

2.1. Raw materials and experimental methods

The composites are manufactured from unidirectional carbon fiber cloth, epoxy resin and high purity Zirconium tungstate ($\text{ZrW}_2\text{O}_8$) particles by using compression molding technique. The 12 K unidirectional T700 carbon fiber cloth produced by Toray are used, in which the areal density is 200 g cm$^{-2}$ and the warp and weft densities are 2.5 yarns/cm. The matrix used is E51 epoxy resin and the curing agent used is 593 curing agent produced by Shanghai Aotunhuagong Co., Ltd The diluent is anhydrous ethanol. The chemical composition of $\text{ZrW}_2\text{O}_8$ particles (Shanghai Dianyang Industrial Co., Ltd) is given in table 1.

The process of preparing $\text{ZrW}_2\text{O}_8$-C/E51 composites is illustrated in figure 1. The first step is to mix $100 \text{g}$ E51 epoxy resin with the different proportion of diluent, and then stir the mixture for 2–10 min The second step is to dry the $\text{ZrW}_2\text{O}_8$ particles in a vacuum drying oven and to add them to the mixed liquid, and then stir the mixture for 2–10 min In the next step, add 25–50 g 593 curing agent to the mixture, mix the mixture mechanically (2–10 min) and place it in an ultrasonic cleaner at the room temperature for 10–20 min The uncured mixture of resins and particles is vacuumed (1–5 min) to remove the air bubbles before being spread on the fabrics.

The curing mixed solution is spread on both sides of the carbon fiber cloth sheets before lamination (Carbon fiber volume fraction is about 30%). The uncured laminate is vacuumed to remove the air bubbles for 5–30 min. At the same time, the curing reaction of composites is carried out (at room temperature). Then, the carbon fiber lamination is put into a pressing mold to achieve pressure curing process. After the resin fully cured, $\text{ZrW}_2\text{O}_8$-C/E51 composite is obtained.

| Item | Unit | Purity (Wt%) | Particle size (D50) (μm) | Al (Wt%) | K (Wt%) | Ca (Wt%) | Fe (Wt%) | Ni (Wt%) | Cu (Wt%) | Hf (Wt%) |
|------|------|-------------|-------------------------|---------|--------|---------|--------|--------|--------|--------|
| Result | 99.78 | 0.48 | 0.058 | 0.014 | 0.053 | 0.013 | 0.018 | 0.023 | 0.35 |
2.2. Testing and characterization methods

In order to analyze the properties of the composites, four kinds of samples are prepared: resin sample, resin + particle sample, resin + carbon fiber sample and resin + carbon fiber + particle sample. In order to observe the impregnation microstructures, defect structures and tensile fracture morphology of fabricated ZrW$_2$O$_8$-Cf/E51 composites, the test samples are observed by JEOL JSM-6390A scanning electron microscope (SEM).

The CTEs and tensile strength are tested. The thermal expansion test is carried out according to the standard GB/T 2572, and the thermal expansion behaviors and average CTEs of ZrW$_2$O$_8$-Cf/E51 composites are measured by using DIL 402 C thermal expansion tester. The size of the sample is selected as $\Phi 6$ mm $\times$ 20 mm, and the test temperature ranges from 45°C to 100°C. The tensile test is carried out on a universal tensile testing machine (CMT5304-30KN), and the loading rate is 0.5 mm min$^{-1}$. The tensile specimens are machined to the corresponding dimensions (75 mm $\times$ 10 mm $\times$ 2 mm with a constant span length of 20 mm) according to the standard GB/T 3354.

3. Experimental results and analysis

The composites prepared in this paper contain zirconium tungstate particles, carbon fibers and epoxy resin (figure 2). It can be seen that there exist white particles in the resin and EDS test shows that these white particles are ZrW$_2$O$_8$. The preparation process involves particles dispersion, fiber infiltration, resin curing and other process steps. Each step also concerns a number of process parameters. All these process parameters will affect the preparation quality of the composites. When the process parameters are unreasonable, the defects such as particle agglomeration, non-uniform dispersion, pore, void and so on will appear in the composites. Therefore, it is necessary to conduct in-depth study on the causes of these defects and to develop the methods for reducing and even eliminating the defects and for preparing the ZrW$_2$O$_8$-Cf/E51 composites with ideal microstructures and properties.
3.1. Analysis of particles distribution defects

Figure 3 shows the agglomeration and non-uniform dispersion of ZrW$_2$O$_8$ particles in the resin matrix. The size of large particles reaches about 40 μm (figure 3(a)), which is about 100 times larger than a single particle.

Large particles are formed by aggregation of many individual particles and the bonding strength between individual particles is far lower than that of the matrix resin. When the composites are deformed, these agglomerated large particles will crack and break up. Therefore, these agglomerated large particles will become the source of crack propagation in the composites and reduce the properties of the composites. In addition, the density of ZrW$_2$O$_8$ particle is about 5 g cm$^{-3}$, which is higher than that of matrix resin. So, particle settling will occur during the process of resin curing because of the high gravity of the agglomerated large particles, as shown in the figure 3(b). Through the experiments, we find that the larger the agglomerated particles are, the more significant the settling of particles is. Eventually, a layer consisting of large particles will be formed in the composites. Therefore, the dispersion of ZrW$_2$O$_8$ particles is an important factor affecting the properties of composites.

In order to reduce the particles agglomeration, the drying treatment is carried out before the particles are added. Many studies have shown that it is easy to form liquid bridges between nanoparticles in humid environment [24, 25]. The liquid bridge force is very strong, which can easily cause the particle agglomeration, i.e., dispersion difficulty. The drying treatment can effectively prevent and destroy the liquid bridge between particles, which makes the particles more easily dispersed.

Another reason for particle agglomeration is that ZrW$_2$O$_8$ particles used in this study have small size which is about 0.48 μm. Because of the small particle size, ZrW$_2$O$_8$ particles have large specific surface area and high surface energy, which are easy to cause particles to attract each other and agglomerate [26]. In order to reduce the particle agglomeration, a method combining mechanical stirring with ultrasonic vibration is adopted in this study. Ultrasonic vibration can destroy the large particles formed by particle agglomeration and scatter them into many single particles. Then the particles are evenly dispersed in the resin matrix by mechanical stirring. Through the experiments, we find that too long or too short mechanical stirring and ultrasonic vibration time are harmful to the preparation of ZrW$_2$O$_8$-C$_f$/E51 composites. If the mechanical stirring or ultrasonic vibration time is too short, the particle agglomeration cannot be eliminated. If the mechanical stirring or ultrasonic vibration time is too long, the curing rate of the resin will be affected. Therefore, the optimal mechanical stirring and ultrasonic vibration time should be determined through experiments.

![Figure 3. Particle distribution defect.](image_url)

![Figure 4. Microstructure of ZrW$_2$O$_8$-E51 composite without defects.](image_url)
vibration time is too long, the mixture will increase in viscosity as a result of the increase of the curing reaction. Increased viscosity will make it more difficult for fibers to infiltrate. Through experiments study, we find that after adding 9% particles the ideal ZrW$_2$O$_8$-E51 mixture can be made by using the mechanical stirring time of 15 min, ultrasonic vibration time of 15 min and vacuum defoaming time of 3 min. The cured microstructure of the ideal ZrW$_2$O$_8$-E51 mixture is shown in figure 4, which implies that the particles are uniform in size and dispersion, and that no large particles or settling of particles are observed.

### 3.2. Analysis of impregnation defects

In the process of impregnating carbon fibers with the mixture of particles and resin, the fabrication defects of the composites will be induced if the process parameters are unreasonable. Figure 5 presents the microstructures of the ZrW$_2$O$_8$-Cf/E51 composites with impregnation defects.

As shown in figure 5(a), there are pores in the composites. In the process of resin impregnating carbon fibers, a certain number of bubbles will be formed between the fibers. If these bubbles do not overflow the composites before the resin being fully cured, they will form the pores. Due to the existence of pores, stress concentration will occur, which accelerates the failure of the composites. So, the pores in the composites will not only affect the CTEs of the composites, but also reduce the mechanical properties of the composites. In order to reduce or eliminate this defect, the proportion of resin, diluent and curing agent is studied to control the viscosity and curing time. Long curing time and good fluidity of resin are beneficial for bubble overflow. So, the numbers of pores in the composites decrease with the curing time prolonging and the viscosity decreasing. However, for the ZrW$_2$O$_8$-Cf/E51 composites studied in this paper, long curing time and low viscosity can cause particle settling and accumulating on the surface of the fibers, as shown in figure 5(b).

When the ratio of resin, diluent and curing agent is 5:1:1, the curing time and viscosity of resin (about 7600 mPa.s at 25 °C) are feasible. Figure 6 shows the microstructure of the ZrW$_2$O$_8$-Cf/E51 composites prepared by these parameters. Figure 6(a) shows that the fibers and particles are evenly distributed. There is no obvious pore in the resin or between the fibers. In addition, there is no large aggregation or settling of particles. Figure 6(b) shows that ZrW$_2$O$_8$ particles can enter the gaps among the fiber bundles. Figure 6(c) shows that the interface between the fiber and resin is well bonded and particles can embed in the resin between fibers.
3.3. Thermal expansion and strength of ZrW2O8-Cf/E51 composite

Figure 7 shows the thermal expansion behaviors of different composite samples. It can be seen that the CTE of E51 resin is improved with the addition of carbon fibers and ZrW2O8 particles. When both carbon fibers and ZrW2O8 particles are added, the composites show the lowest CTE. The CTE of the resin after adding 9% particles is about $56.0 \times 10^{-6}$/°C which is 23% less than that of pure resin. The decrease of the CTE after the ZrW2O8 particle addition is mainly due to two reasons. One is the negative CTE of the ZrW2O8 particles. The other is that the ZrW2O8 particles are closely bound to the epoxy resin matrix which can effectively prevent the thermal expansion of the matrix. Figure 7 also presents that the CTE of the composites is about $8.0 \times 10^{-6}$/°C, which decreases after the addition of carbon fibers. The reason is that the carbon fibers have the characteristic of negative CTE in the axial direction and are continuous inside the composites. Moreover, under the combined effect of the carbon fibers and ZrW2O8 particles, the lowest CTE of $-0.52 \times 10^{-6}$/°C is obtained for the ZrW2O8-Cf/E51 composites.

Figure 8 shows the tensile strengths of the different composites. It can be seen that the mechanical properties of the E51 resin are improved with the fibers and particles addition. When both fibers and particles are added, the composite has the highest strength, which is about 440 MPa.

As figure 8 shown, the strength of the epoxy resin without particles is 21 MPa. When the particles (9%) are added, the strength increases to 36 MPa. As a discontinuous reinforcement, micro-particles have been extensively studied in improving the mechanical properties of composites. When the particles reinforced composites are subjected to external loading, the load is transferred from the matrix with lower elastic modulus to the hard reinforced particles with higher elastic modulus. The load is transferred and the reinforced particles become the loading body, which strengthens the matrix. This strengthening mechanism has also been confirmed by the works [26, 27].
After the carbon fibers are added, the ultimate tensile strength of the composites increases to 321 MPa, which is greatly improved. Because the carbon fibers have high strength and high elastic moduli, the axial tensile strength even can reach 3500 MPa. When the composites are subjected to tensile load, the matrix resin can transfer the load to the carbon fibers, which play a major role in bearing loads \cite{28, 29}. So, the mechanical properties of the composites can be greatly improved after the addition of the carbon fibers.

4. Conclusions

Based on the experimental observations and analyses, the following conclusions are obtained:

(1) The ZrW2O8-Cf/E51 composites with negative CTEs are fabricated. The experimental results confirm that the CTE and tensile strength of E51 resin are improved with the addition of the carbon fibers and ZrW2O8 particles. When both the carbon fibers and ZrW2O8 particles are added, the composites show the lowest CTE which is about $-0.52 \times 10^{-6}/^\circ C$ and the highest strength which is about 440 MPa.

(2) Because of the small size of the particles, the particles agglomeration or settlement would occur if the process parameters are not controlled properly. To reduce the particles agglomeration, a method combining mechanical stirring with ultrasonic vibration is adopted and ZrW2O8-E51 mixture can be made by using the mechanical stirring of 8 min, ultrasonic vibration time of 15 min and vacuum defoaming time of 4 min.

(3) Long curing time and good fluidity of resin are beneficial for resin impregnating the carbon fibers and bubble overflowing. However, for the ZrW2O8-Cf/E51 composites studied in this paper, long curing time and low viscosity can cause particle settling and accumulation. When the ratio of resin, diluent and curing agent is 5:1:1, the curing time and viscosity of resin are feasible.

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