Preparation and Properties of Needle-punched Woven Quartz Fiber Reinforced SiO$_2$ Ceramic Matrix Composites

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Abstract. The needle-punched woven silica fiber reinforced SiO$_2$ ceramic matrix composites were prepared by liquid phase infiltration-in-situ solidification molding process. The prepared composites have high density and good uniformity, and the mechanical properties of the composites at room temperature. Microstructure, interfacial properties and dielectric properties at room temperature were investigated, and the strengthening and toughening mechanism of acupuncture-woven quartz fiber reinforced SiO$_2$ ceramic matrix composites was discussed. The mechanical properties at room temperature show that the tensile strength, flexural strength, compressive strength and interlaminar shear strength of the composites reach 35.6MPa, 79.0MPa, 122.0MPa, 11.9MPa, respectively. Scanning electron microscopy (SEM) and energy spectrum of the fractures of the samples (EDS) observation and analysis showed that there was no interfacial reaction between the matrix and the fiber, and the interface was suitable. The main factors that improve the mechanical properties of composite materials at room temperature are crack steering, expansion barriers, and fiber pull-out. The dielectric properties of the composite at room temperature do not change or change much under different X, Ka, and Ku conditions. As the bulk density increases, the dielectric constant of the composite increases gradually, and the loss tangent is always maintained at $10^{-3}$ orders of magnitude.

1. Introduction

Since the mid-to-late 1980s, the research on fiber-reinforced and toughened ceramics has become a frontier and hot spot in the research and development of tech ceramics, and has been highly valued by countries all over the world. Compared with particle-reinforced ceramic materials, fiber-reinforced ceramic-based composite tree materials have better mechanical and thermal shock resistance. The fiber reinforced and toughened ceramic matrix composite tree material is used for preparing the radome, which not only has better strength, but more importantly, greatly improves the structural reliability and thermal shock resistance of the radome, and is an important development direction of heat-resistant radome material. Considering the special requirements of the electrical properties of the material, it can be used as a reinforcing fiber with glass fiber, SiO$_2$ fiber, Si$_3$N$_4$ fiber, BN fiber, etc. It is easy to obtain and has excellent performance. The continuous fiber suitable for the radome is only glass fiber and quartz fiber. Both the United States and the former Soviet Union used glass fiber reinforced tree materials to prepare radomes. Examples include the US "Hock" missile and the former Soviet Union's SA-6 missile. However, glass fiber has the disadvantages of low softening temperature and low modulus, which is not suitable for the manufacture of Mach number missile radome$^{[1,2]}$. The dielectric
constant and loss tangent of quartz fiber do not change substantially in a wide frequency range, and the quartz fiber has good chemical stability, thermal shock resistance, ablation resistance, good flexibility, easy braiding, and excellent dielectric properties. It is very suitable for applications in the wave-transparent field such as aviation and aerospace. It is also the most used reinforcing fiber in the wave-transparent composite materials abroad\cite{3-4}.

The manufacture of low-cost radomes mainly includes both materials and manufacturing techniques. At present, the material units with mature domestic technological conditions are mainly two units of Wuhan Xinyoutai and Hubei Feilihua. The cost of raw materials is basically fixed, so the low-cost radome is currently considered to reduce the manufacturing technology without significantly reducing the mechanical properties. 3D weaving technology can profile various structural prefabricated parts, multi-round composite of pre-formed parts, and then realize the final shape and composite material products satisfying different size requirements through precision machining. 3D woven composite materials are getting more and more aerospace. The department welcomes and attaches importance, but the high cost, complicated process and slow speed of 3D weaving technology make the wide application of 3D weaving technology hindered. The 2.5D woven composite material avoids the poor performance between the woven composite layers, solves the complicated shortcomings of the 3D woven composite material process, reduces the manufacturing cost and shortens the production cycle\cite{5}, but the preform requires a large amount of artificial assisted weaving, and the preparation cycle Still relatively long, the price is still relatively expensive. With the development of fiber weaving technology, the low-cost needle-punched preforms have greatly reduced the production cost of quartz fiber reinforced ceramic matrix composites, mainly because the needle-punched structure is mainly machine-woven, with little manual assistance, and the production cycle. It has also been greatly shortened, thus providing a possibility for the wide application of the material in the field of radomes. Acupuncture is a mechanical method of reinforcing the fiber web. The mechanism of the needle punching is to use the thorns with a triangular shape (or other form) and hooks on the edges to repeatedly puncture the fiber web under controlled conditions. The effect of the hook on the needle causes the fibers in the fiber web to be hooked in the vertical direction, so that the original loose fibers of the fiber web are entangled to form a relatively tight and strong nonwoven fabric\cite{6}.

The liquid phase infiltration-in-situ solidification molding process is a more effective and convenient forming method for manufacturing fiber reinforced ceramic matrix composite materials, and has the advantages of short process cycle, high degree of densification, good uniformity and low cost. It is a silica sol with high fluidity and high solid content, which is infiltrated into the fiber braid to produce in-situ solidification, thereby improving the density and uniformity of the composite. In this experiment, a needle-punched woven silica fiber reinforced SiO\textsubscript{2} ceramic matrix composite was prepared by liquid phase infiltration-in-situ solidification molding process. The mechanical properties, microstructure, interfacial properties and strengthening and toughening mechanism of the composite were investigated. Dielectric properties were studied and analyzed.

2. Experiment

2.1. Fiber preform structure selection
The fiber preform is designed according to different environmental conditions, mainly by adjusting the yarn specification and linear density, the structure of the quartz fiber cloth, the warp and weft density, the areal density, the cloth thickness, the tread density, the density between the cloth and the mesh layer, bulk density and other parameters, weaving a prefabricated body that can meet the requirements of use, where in the adjustment of density parameters between warp and weft density, cloth and mesh layer has a great influence on liquid phase infiltration, and the three parameters are unreasonable and will directly affect the penetration into the silica sol does not achieve the purpose of high degree of densification and homogenization. Therefore, it is necessary to design a reasonable parameter to ensure the best effect of the percolation. In this experiment, a needle-punched woven structure
prefabricated body made of quartz cloth and net tire is used. The weft density of the fabric is 6~10 pieces/cm, the interlayer density is 7~12 layers/cm, and the fabric fiber volume content is 28%~40%.

2.2. Main raw materials for the experiment
The main raw material is silica sol.

2.3. Experimental method
Firstly, the pre-formed fabric of quartz fiber is pretreated to remove the organic matter on the surface of the fiber, so that the silica component on the surface of the fiber is completely exposed, thereby ensuring that the interface can form a certain bonding force when the fabric is combined with the silica sol, and the organic matter is removed. It can ensure the damage of the fiber surface is minimized. Secondly, the silica sol is pretreated. The concentration, viscosity, particle size and impurity content of the silica sol must be strictly controlled within a certain range. The main purpose is to ensure the performance of the final product.

According to the experimental design, a certain concentration of silica sol is injected into the quartz fiber preform through vacuum, vibration and pressure in the liquid phase infiltration-in-situ solidification molding process. After in-situ curing, it passes 400℃ to 1050℃. Heat treatment, repeated 3 to 5 rounds of composite infiltration - in-situ curing, to meet the performance requirements of product design requirements.

2.4. Test
The Model 5928 ceramic universal material testing machine was used to test the mechanical properties at room temperature, including tensile strength, flexural strength, compressive strength, tensile strength. Sample size: 120 mm × 20 mm × 10 mm, loading rate 0.5 mm / min, three points Bending strength sample size: 80 mm × 10 mm × 10 mm, span 65 mm, loading rate 0.5 mm / min, compressive strength sample size: 25 mm × 10 mm × 10 mm, loading rate 0.5 mm / min . The fracture surface microscopic morphology was observed by Hitachi SU8010 scanning electron microscopy (with energy spectrum analysis). The dielectric properties at room temperature were tested by short-circuit waveguide method, and the sample size was selected according to different bands.

3. Results and discussion
3.1. Normal temperature mechanical properties of composite materials
The room temperature tensile strength, room temperature bending strength and room temperature compressive strength of acupuncture-woven quartz fiber reinforced SiO₂ ceramic matrix composites are shown in Fig.1. From the test results, the room temperature tensile, compression, bending and interlaminar shear of the composite material The maximum shear strength reached 35.6MPa, 79.0MPa, 122.0MPa, and 11.9MPa, respectively, and the data dispersion was relatively small. Compared with the normal temperature stretching of the acupuncture quartz fiber preform reinforced quartz ceramic composite reported in[4], the strength is 31.8MPa and the compressive strength is 88.8MPa. At present, there are few reports on data at home and abroad. From the published literature, the ceramic matrix composites meet the requirements of the current aerospace sector in terms of composite processes, mechanical properties at room temperature, dielectric properties, and production costs.
3.2. Fracture morphology of composite materials

Fig. 2a is the bending fracture morphology of the needle-punched woven quartz fiber reinforced SiO$_2$ ceramic matrix composite. It can be seen from Fig. 2a that the fiber is pulled out obviously when the composite is broken, and the fiber is extracted and consumes more energy, and the composite is bent. The increase of strength plays a positive role. The existence of fiber really plays an important role. At the same time, from the load-displacement curve of the needle-punched woven quartz fiber reinforced SiO$_2$ ceramic matrix composite of Fig. 3, it can be seen that when the composite material starts to force, the law of load and displacement is basically a linear relationship. When the maximum load is reached, the displacement curve begins to change, showing a step-down trend, indicating that the quartz fiber plays a good role in strengthening. The presence of quartz fiber offsets most of the force. The effect of the composite material has a significant effect on the improvement of the mechanical properties of the composite material. The fracture of the composite material is non-brittle fracture.

3.3. Interface and strengthening mechanism of composite materials

Generally, the properties of fiber-reinforced ceramic matrix composites are determined by the properties of the fibers, matrix, and their interfaces[7], where interface characteristics have a greater impact on material properties. The interface bonding strength controls the energy absorption mechanism. Interface debonding, crack steering, branching and fiber extraction all contribute to the improvement of fracture toughness of ceramic matrix composites. The interface bonding strength is too high, and it is not easy to cause fiber debonding and pulling out. The material is prone to brittle fracture. If the interface bonding strength is too low, the fiber can not effectively transfer the load. Only when the interface bonding strength is moderate, the fiber can effectively transfer the load. It can also produce a certain degree of debonding and extraction, so that the strength of the composite material is improved[8].
Figure 3. The load-displacement curve of needle-punched woven quartz fiber reinforced SiO$_2$ ceramic matrix composite.

Figure 4. EDS spectrum analysis of interface of needle-punched woven quartz fiber reinforced SiO$_2$ ceramic matrix composites.

It can be seen from Fig.2a and Fig.2b that the fibers arranged in the needle-punched woven quartz fiber reinforced SiO$_2$ ceramic matrix composite are evenly arranged. When the composite loading load, it can be observed from the fiber axial direction that the fibers and the matrix are separated, and the separation will be absorbed. The more energy, that is, the presence of the fiber, causes the crack to be steered under load, and the turning and spreading of the crack is hindered by the presence of high-strength fibers, thereby improving the overall mechanical properties of the composite. Furthermore, the density of the composite material is increased between the matrix-filled fibers. When the fibers are pulled out, the fiber pull-out is hindered due to a certain degree of combination of the matrix and the fibers, which further improves the mechanics of the composite material to some extent.

It can also be seen from Fig.2b that the surface of the reinforcing fiber is relatively smooth, indicating that the composite preparation process is reasonable, and there is no fiber damage caused by the fiber over-burning phenomenon, firstly ensuring that the fiber reinforcement is not weakened.

The energy spectrum analysis of Fig.4 shows that the main components in the needle-punched woven silica fiber reinforced SiO$_2$ ceramic matrix composite are Si and O. No other components are found, indicating that no interfacial reaction occurs in the needled quartz fiber reinforced SiO$_2$ ceramic matrix composite. The load-displacement curve of Fig.3 also shows that the fracture mode is not brittle fracture, which indicates that the interface strength between the fiber and the matrix is moderate, the fiber effectively transfers the load, and the fiber is debonded and extracted, further improving the mechanical properties of the composite.

3.4. Room temperature dielectric properties of composite materials

Dielectric properties are the most important indicators for evaluating the performance of a wave-transparent material. They usually include two parameters: dielectric constant $\varepsilon$ and loss tangent $\tan\delta$. In general, in the frequency range of 0.3~300GHz, the suitable dielectric constant $\varepsilon$ of the wave-transparent material is 1~4, and the loss tangent $\tan\delta$ is on the order of $10^{-1}$~$10^{-3}$, so that the desired wave transmission performance can be obtained. And smaller insertion loss$^{[9]}$. Table 1 shows the bulk density and dielectric value of the composite under normal temperature conditions. The dielectric sample test is in the frequency range of different bands. As can be seen from Table 1, the dielectric properties of the composite are good, and the dielectric constant is in Ku. In the frequency range of X and Ka, the values do not change much, and are concentrated between 2.70~3.05, which indicates that the dielectric constant and loss tangent of quartz fiber change less in a wider frequency range under normal temperature conditions. SiO$_2$ ceramic matrix composite basically meets the requirements of the wave transmission performance in the frequency range of 0.3~300GHz.
Tab.1 Bulk density and dielectric constant and loss tangent tģ spectral value of needle-punched woven quartz fiber reinforced SiO₂ ceramic matrix composites

| Bulk density (/ g·cm⁻³) | Dielectric constant ((Ku band) | Loss tangent ((Ku band) | Dielectric constant ((X band) | Loss tangent ((X band) | Dielectric constant ((Ka band) | Loss tangent ((Ka band) |
|------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------|-------------------------------|-------------------------|
| 1.55                   | 2.70                          | 4.7×10⁻³                | 2.71                          | 3.2×10⁻³                | 2.69                          | 3.9×10⁻³                |
| 1.60                   | 2.79                          | 3.5×10⁻³                | 2.80                          | 4.3×10⁻³                | 2.78                          | 4.1×10⁻³                |
| 1.65                   | 2.88                          | 3.9×10⁻³                | 2.89                          | 5.2×10⁻³                | 2.90                          | 4.3×10⁻³                |
| 1.70                   | 2.96                          | 4.2×10⁻³                | 2.95                          | 5.3×10⁻³                | 2.95                          | 3.9×10⁻³                |
| 1.72                   | 3.05                          | 2.8×10⁻³                | 3.04                          | 1.7×10⁻³                | 3.06                          | 3.7×10⁻³                |

4. Conclusion

4.1. In this experiment, a needle-punched woven silica fiber reinforced SiO₂ ceramic matrix composite was prepared by liquid phase infiltration-in-situ solidification molding process. The prepared composite material had high density and good uniformity, and mechanical properties at room temperature. The test shows that the maximum tensile strength, bending strength, compressive strength and interlaminar shear strength of the composites are 35.6MPa, 79.0MPa, 122.0MPa and 11.9MPa, respectively.

4.2. The main factors that improve the mechanical properties of composite materials at room temperature are crack steering, expansion barriers, and fiber pull-out.

4.3. The dielectric properties of composites at room temperature are small under different conditions of X, Ka and Ku, and are concentrated between 2.70 and 3.05. With the increase of bulk density, the dielectric constant of composites increases gradually, and the loss tangent is always stay on the order of 10⁻³.

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