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Research Progress of Ceramic-based Absorbing Composite Materials

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Abstract: Absorbing materials can convert electromagnetic energy into other forms of energy. In recent years, ceramic-based absorbing composite materials have received widespread attention from researchers in many fields, such as mobile communications and military technology due to their excellent performance in corrosion resistance and stability, and have extremely broad application prospects. This article first briefly describes the structure and absorption principle of ceramic matrix composite absorbing materials. Then the research progress of ceramic-based absorbing materials in recent years was reviewed, including the preparation processes and advantages and disadvantages of various ceramic substrates. Finally, we review the practical application scenarios of this material and discuss future research directions and urgent problems to be solved.

Keywords: Absorbing materials, ceramic-based absorbing composite materials, electrical loss, magnetic loss, sandwich shell structure.

1. Introduction

With the application of the latest generation of communication technology, the diversification of communication equipment and wave bands has led to an increasingly complex electromagnetic environment, which has a great impact on precision measurements in the deep space field. In addition, entering the 21st century, radar technology is the latest and most important information detection method on the military battlefield. Radar can provide us with detailed information about the enemy, which can gain huge advantages in the early stages of modern war. Therefore, while developing new military radars, stealth technology that can counter radar detection is also the focus of development in various countries[1].

Absorbing materials are a type of material that can attenuate electromagnetic waves and reduce radar reflection. According to the different molding processes and functional structures, they can be roughly divided into two categories: one is traditional covering absorbing materials, such as ferrite powder, metal powder, etc. However, in recent years, due to its shortcomings such as its large weight, poor stability, and easy separation of the matrix, the use areas and conditions of the material have been greatly restricted[2]. The other type is structural absorbing material, which consists of two parts: absorbing agent and matrix. This type of material achieves structural and functional integration while taking into account excellent mechanical properties and wave-absorbing properties.

With the rapid development in the field of materials, new materials such as ceramics that are corrosion-resistant, high-temperature resistant, and affordable have entered people's attention[3]. Ceramic-based absorbing composite materials are composed of two parts: absorbing agent and ceramic matrix. In recent years, the focus of research has been to use simulation computing technology to design more reasonable structures while giving full play to the role of materials. By changing the structural design, the impedance performance of the material can be improved and the wave-absorbing performance of the material can be further fully utilized.

2. Principle of Absorbing Materials

When the electromagnetic wave reaches the surface of the material, part of the electromagnetic wave is reflected and the other part enters the interior. Since the molecules of traditional materials are densely arranged, very little light enters the interior, so most of the light is returned. This is how radar detects objects. The absorbing material has a loose and porous structure, which is prone to reflection, scattering or transmission within the material structure, thereby dissipating radar wave energy and minimizing the reflection of radar waves, which makes it difficult for the receiver to accept the reflected signal.

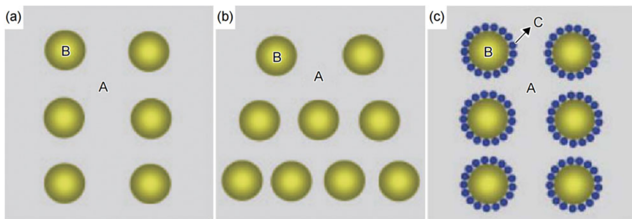

Figure 1. Microstructure of absorbing composite materials (a) A/B type, (b) gradient type, (c) A/B/C type

During this process, the energy of electromagnetic waves is greatly attenuated, thereby achieving the effect of invisibility. According to previous research, we know that the attenuation mechanism of electromagnetic waves includes magnetic loss and electrical loss. The changes in magnetic susceptibility and dielectric constant can reflect the processes of magnetization and polarization of materials respectively.

2.1. Magnetic loss

Magnetic losses mainly include hysteresis loss, eddy current loss and natural resonance in electromagnetic wave absorption. Hysteresis loss refers to the energy dissipation that occurs after the magnetic moment and magnetic domain wall displacement occur when the direction of the external magnetic field changes. Eddy current loss refers to the energy consumption phenomenon of induced current caused by alternating magnetic field. In addition, the size of the attenuation coefficient also indicates the quality of the wave absorption performance:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon''-\mu'\varepsilon') + \sqrt{(\mu''\varepsilon''-\mu'\varepsilon')^2 + (\mu'\varepsilon''+\mu''\varepsilon')^2}} \quad [4] \ (1)$$

2.2. Electrical loss

Electrical losses include conductivity losses and polarization losses. Conductivity loss refers to the fact that a part of the carriers in the electric field form a current and are dissipated as they pass through. Polarization loss is the result of the joint action of ions, electrons, and dipole plasma.

2.3. Impedance matching

Impedance matching refers to adjusting the input impedance and output impedance to make the electronic device meet certain conditions. Theoretically, the condition for impedance matching is to maximize the transmission power of the system or minimize signal reflection. The design goal of absorbing materials is to allow radar waves to be quickly absorbed when projected onto the surface of the absorbing material, and to quickly convert radar waves into heat or other forms of energy inside the material, thereby reducing radar wave reflection. According to the impedance matching formula[5]:

$$Z_{in} = Z_0 (\frac{\mu_r}{\varepsilon_r})^{1/2} Tanh[j(2\pi f d(\mu_r \varepsilon_r)^{1/2}/c)] \quad (2)$$

$$\Gamma = (Z_{in} - Z_0)/(Z_{in} + Z_0) \quad (3)$$

In the formula: Z_0 and Z_{in} are the standardized impedances of air and absorber respectively, ε_r and μ_r are the complex dielectric constant and complex permeability of the absorber respectively, f is the electromagnetic wave frequency, and d is the thickness of the absorber, c is the speed of light, Γ is the reflection coefficient. It can be seen from the above formula that when $\varepsilon_r = \mu_r$, $Z_0 = Z_{in}$, the impedance of the absorber is equal to the impedance of the air, that is, the impedance matches. At this time, the reflection coefficient $\Gamma = 0$, which means that the impedances are matched at this time, the least electromagnetic waves are reflected, and the most electromagnetic waves are absorbed by the material. With the deepening of research in recent years, scholars have found that it is difficult to achieve impedance matching for most materials without modification, and it is also very difficult to achieve complete absorption of waves by the material. Therefore, preparing composite materials or modifying original materials has been the focus of research by scholars in recent years. This article takes ceramic-based absorbing composite materials as an example to conduct a review study in this field.

3. Classification of Absorbing Materials

3.1. Magnetic metal-based absorbing materials

Magnetic metal is one of the traditional wave-absorbing materials. Its surface is loose and porous, including Fe, Ca, Ni, etc. Gao et al. used a heat-assisted surface attachment process to synthesize Fe/SiC composites with adjustable core-shell structure[6]. The effective absorption bandwidth is 7.60 GHz, minimal reflection loss -51.0 dB (2.01 mm). Li et al. loaded short and thin carbon nanotubes (NCNTs) coated with magnetic Co particles on hollow nanoplates (HCNPs)[7]. Co@HCNP/NCNTs assembled from 0D, 1D and 2D nanostructures have a three-dimensional interconnected grid structure and rich interface defects. TThe material has an effective absorption bandwidth of 4.26 GHz and a reflection loss of -41.08 dB (2.00 mm), which is a very excellent performance. Cheng et al. loaded the magnetized Ni-Flower/MXene composite material on the surface of melamine foam through electrostatic self-assembly and dip coating adsorption process, and the reflection loss was -62.7 dB (2.00 mm), effective absorption bandwidth 6. 88 GHz (1.80 mm)[8].

3.2. Carbon-based absorbing materials

In recent years, carbon and its derivatives have become popular among new wave-absorbing materials due to their excellent properties such as high surface properties, high strength-to-mass ratio, corrosion resistance, and ultra-high carrier mobility. In particular, the invention and introduction of MXene has greatly promoted the development of this field. Zhang et al. used a template-assisted method to prepare carbon hollow microspheres (PCHM) with uniform mesoporous shells . The minimum reflection loss is -39.4 dB, and the widest effective absorption bandwidth is 5.28 GHz[9]. With operation and impedance matching, minimum reflection loss (RL) and EAB reach -51.7 dB and 6.00 GHz respectively.

3.3. Metal oxide based absorbing materials

Metal oxide-based absorbing materials mainly include Fe2O3, Fe3O4, Al2O3, ZnO, etc., from which ceramic-based absorbing composite materials are derived. Liang et al. used a simple hydrothermal method to synthesize precursor carbon fiber (SCF)@Fe_3O_4@FeO honeycomb composites (calcined at 700°C, 1.90 mm, 6.10 GHz, -40.8 dB)[10]. Zhu et al. developed Co/ZnO graphene composite materials. Graphene sheets are used as lightweight and strong scaffolds. The minimum reflection loss value of this material is -51.1 dB, and the effective absorption bandwidth is 4.70 GHz[11].

3.4. Other types

With the rapid development of this field in recent years, there are many new types, for example: metal organic frameworks (MOFs)-based absorbing materials, layered double metal hydroxides (LDHs)-based absorbing materials, conductive polymer-based absorbing materials, etc.

4. Ceramic-based Absorbing Composite Materials

Unlike ordinary absorbing materials that directly coat absorbing agents and adhesives on the surface of the structure, ceramic-based absorbing composite materials combine the two. It consists of two parts: absorber and matrix. Absorbers further enhance electromagnetic losses through material properties. As mentioned above, most ceramic materials are materials with low dielectric constant and low dielectric loss, and have good wave transmittance and mechanical strength, such as Al_2O_3, Si_3N_4, etc.

In recent years, with the development of topology and structural mechanics, some scientists have significantly improved its toughness by designing microstructures and macrostructures, such as fiber structures, sandwich shell structures, etc. In addition, a multi-layer structure can be used to obtain better effects through field superposition. This not only improves the hardness and brittleness of ceramics and optimizes their wave-absorbing properties, but also further develops the wave-absorbing properties of ceramic materials.

4.1. Absorber

Absorbing agent is an important component of absorbing materials. It can be roughly divided into: electrical loss absorbers and magnetic loss absorbers. Common electrical loss absorbers are mainly carbon and carbides, such as pyrolytic carbon, carbon fiber, graphene, carbon nanotubes, SiC, etc. Carbide absorbers have better stability and higher strength than carbon materials. At the same time, the special structure of SiC can also improve the mechanical properties of the ceramic matrix, making it better in bending strength, and make it have better wave absorption performance.

Magnetic loss agent refers to a type of material with higher magnetic permeability and lower dielectric constant. However, it loses its magnetism when the temperature is higher than the Curie temperature, and the modified material also has the disadvantages of poor corrosion resistance and increased weight, making the use conditions of this type of material more stringent. Iron, nickel, cobalt and their composite alloys are common magnetic loss agents. In recent years, ferrite has received great attention due to its high temperature resistance, easy preparation, and dielectric properties that are better than ordinary metals.

4.2. Ceramic matrix

Ceramic substrates vary according to structure. It can be roughly divided into: homogeneous ceramic-based absorbing materials, dispersed phase-enhanced ceramic-based absorbing materials, porous ceramics and honeycomb absorbing materials and other types[12].

4.2.1. Homogeneous ceramic-based absorbing materials

Homogeneous ceramic-based absorbing materials refer to absorbing materials made from a single material through a special process. At present, ceramic-based absorbing materials with SiC as the main component are commonly used. SiC is a wide bandgap semiconductor material. In recent years, researchers have modified it through element doping to give it ideal wave-absorbing properties. Li et al. summarized the dielectric properties of doped modified silicon carbide absorbers . The results show that the doping of elements such as Al, Fe, Ni, and N tends to increase the dielectric constant of SiC, while the doping of B elements reduces the dielectric constant of SiC[13]. This provides a reference template for subsequent research on SiC ceramic dielectric property control and impedance matching.

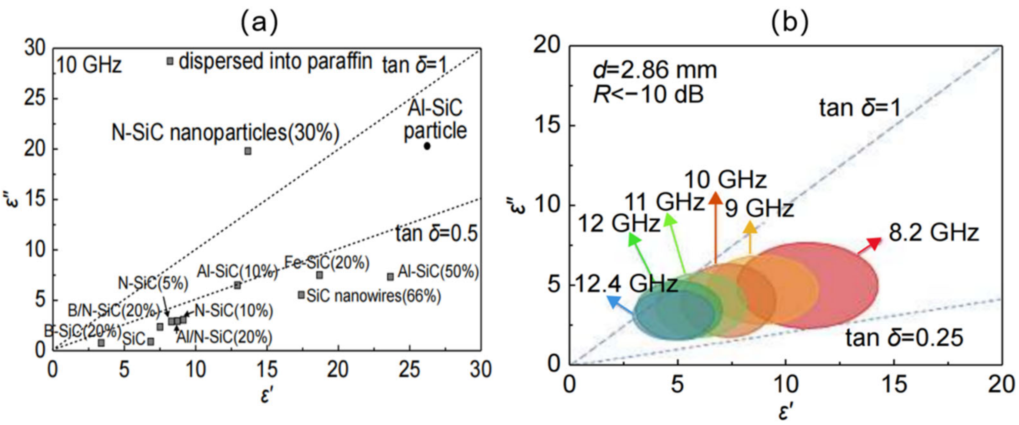

Figure 2. (a) Dielectric properties of doped modified SiC ceramic powder
(b) Range of dielectric constant corresponding to reflectivity R< −10 dB at different frequencies when the thickness is 2.86 mm

4.2.2. Dispersed phase enhanced ceramic-based absorbing materials

Dispersed phase reinforced ceramic-based absorbing materials refer to multi-phase ceramic absorbing materials containing two or more phases, and at least one of the reinforcing phases is a discontinuous phase. The dispersed phase can play a role in toughening the material and enhancing its absorbing properties.

4.2.3. Porous structure ceramic-based honeycomb absorbing material

Porous ceramics are a new type of structure developed in recent years. New ceramic materials with a large number of pores have the characteristics of low density and good thermal insulation performance. In recent years, it has been widely used in thermal insulation, thermal insulation and other fields. Compared with ordinary two-dimensional materials, porous materials have better impedance matching with free space, making it easier for electromagnetic waves to enter the interior of the absorbing material. In porous materials, electromagnetic waves can produce multiple scattering and refraction between pores, which increases the oscillation loss of electromagnetic waves within the material and is conducive to the rapid dissipation of electromagnetic waves within the material.Mei et al. used ceramic 3D printing combined with chemical vapor deposition to prepare porous Al_2O_3/SiC ceramic honeycombs with specific structures[14]. The wave absorption performance of the material can be optimized through the design of the inner corners of the honeycomb. When the channel angle is 30°, the lowest reflectivity of the material can reach –63.65 dB, which is an extremely excellent performance of the honeycomb structure.

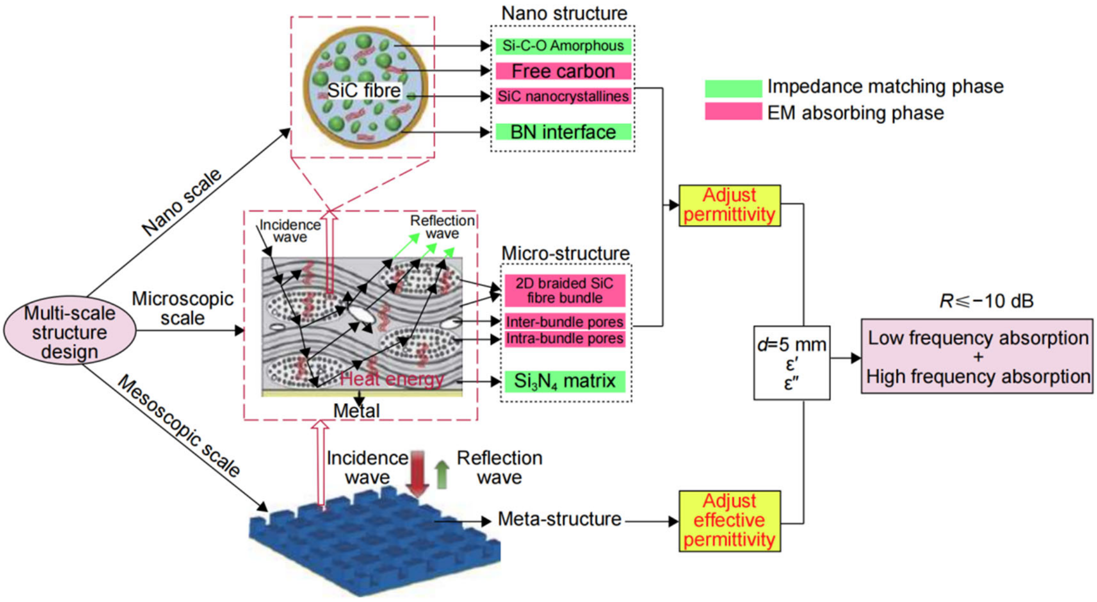

Figure 3. Multi-level structure of SiC_f/Si_3N_4 structural absorbing composite materials

5. Summary and Outlook

This article summarizes the absorbing principles of ceramic-based absorbing materials and the current status of modification research in recent years. With the rapid development of related fields in recent years, modification research has gradually formed based on element doping, porous structure, multi-layer structure design and other methods. These control methods can maximize the absorbing performance of the original ceramic matrix, greatly improving the research speed and progress in this field.

The research trends and goals of absorbing materials in recent years have always been towards high absorption, high performance, light weight, high temperature resistance and other aspects. Ceramic absorbing materials that take into account both quality and performance perfectly match the above requirements. However, absorbing composite ceramic materials often show an imbalance in mechanical properties and absorbing properties in practical applications, especially the brittleness of ceramics, which greatly limits their application in actual production and life.

Our forecasted future development directions are as follows:

(1) Exploration on the strengthening of low fracture toughness and high bending resistance of ceramic-based absorbing composite materials. In recent years, continuous fiber-toughened ceramics have excellent toughening effects and excellent structural load-bearing performance due to their long internal fibers, which makes the material have bright application prospects in structural mechanics and electromagnetic absorption.

(2) Use three-dimensional modeling and simulation experiments, and with the help of computational science, to accurately control various parameters to design better structures. Many studies have shown that optimizing structural design can maximize the wave-absorbing performance of materials. The rapid development of computer simulation science in recent years can also provide great help in this field.

(3) Exploration of advanced sintering technology. With the continuous improvement of design, many traditional sintering processes are difficult to meet the needs of structural design. At the same time, porosity is also an important indicator to measure material performance and mechanical strength. Therefore, only by improving the sintering process can the design be maximized.

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