Preparation and radar absorptive properties of BaFe$_{12}$O$_{19}$-coated glass fiber

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Abstract: Traditional passive jamming materials such as chaff and foil showed some limitations in use because they can only reflect the electromagnetic wave. Therefore, to develop a kind of absorptive passive jamming material to make up for deficiencies of traditional passive jamming materials and improve the jamming efficiency is of great significance. In this paper, the BaFe$_{12}$O$_{19}$-coated glass fiber, used as a kind of radar absorptive chaff, was prepared by sol-gel dip-coating method. The effects of heat treatment temperature, heat treatment time and coating times on film quality, tensile strength and attenuation efficiency of the samples were discussed. The study shows that an increase of the heat treatment temperature and an extension of the heat treatment time is conducive to the growth of barium ferrite grain, while they would introduce the loss of chaff strength at the same time. In addition, multi-coating process can improve the film quality and attenuation efficiency of the sample. Data show that the 10 times coated samples have a best reflectivity of (15GHz, -6.65dB) and the bandwidth of reflectivity lower than -5dB is 11.8 GHz. According to the test results, the prepared material has certain attenuation efficiency in the range of 2GHz-18GHz, having a high practical value.

1. Introduction
Since World War II, the passive radar jamming technology has been rapidly developed. A series of passive jamming devices, mainly including chaff, infrared bombs, and smoke bombs, have been developed and equipped to the sea, land, air and space combatant platforms[1]. Meanwhile with the development of radar anti-jamming technology, especially the anti-chaff technology, traditional passive jamming materials are easily identified by radar and their operational efficiency has been reduced, which would limit their use. Therefore, to develop an efficient, practical, inexpensive absorptive passive jamming material, make up of the chaff, the smoke, and other conventional passive jamming materials to counter radar detector and multi-mode precision guided weapons, has an
William[2] formed a millimeter wave-screening cloud comprised with an aerosol of fine fibers of a carbon composition, in which the particles are of micron diameter and millimeter length. Xu Yun[3] modified the surface properties of carbon fiber by nitric acid oxidation and in-situ PANI coating methods. And the polyaniline-coated carbon fiber has certain attenuation efficiency in the 3mm and 8mm wave. Wang Bei[4] prepared the carbon fiber/retinyl Schiff base salts composite materials which have an absorption and interference effect for 8mm wave. Chen Xin[5] prepared the nickel coated bamboo fibers as the millimeter wave smoke interfering materials. Han Chao[6] covered the nano wave absorption material on aluminum glass fiber and obtained the millimeter wave absorption chaff. The jamming materials prepared by the above research have a certain jamming effect on the millimeter wave, but the effect is not obvious in the range of 2GHz-18GHz. In this paper, a layer of barium ferrite film was coated on the surface of glass fiber by sol-gel method. And the effects of heat treatment temperature, heat treatment time and coating times on film quality, tensile strength and attenuation efficiency of the BaFe$_{12}$O$_{19}$-coated glass fiber were discussed. According to the test results, the absorptive chaff with certain attenuation efficiency in the range of 2GHz-18GHz has been obtained, and from this work a kind of feasible method to prepare the absorptive passive jamming material has been provided.

2. Experimental procedure

2.1. Synthesis of Sol

First, appropriate amount of citric acid was dissolved in the minimum amount of deionized water. Next, Fe(NO$_3$)$_3$·9H$_2$O and Ba(NO$_3$)$_2$ were added into the prepared aqueous solution, in a Fe/Ba molar ratio of 11.5, as shown in Table 1. It should be mentioned that the molar ratio of C$_6$H$_8$O$_7$/($\text{Fe}^{3+}+\text{Ba}^{2+}$) should be 1.5. Under the condition of rapid mixing, the mixed solution was neutralized to pH 7 by adding aqueous ammonia. Then, appropriate amount of polyethylene glycol was added, stirred evenly and kept there for 1h. After that, the neutralized solution was evaporated by heating at 90°C for 3h in water bath with stirring. As the water evaporated, the solution became viscous and finally formed a transparent sol with a certain fluidity and viscosity.

| Fe$^{3+}$/Ba$^{2+}$ | C$_6$H$_8$O$_7$/M$^{m+}$ | polyethylene glycol(g/L) | PH | T(℃) | T(h) |
|---------------------|--------------------------|--------------------------|----|-------|------|
| 11.5                | 1.5                      | 6.6                      | 7  | 90    | 3    |

2.2. Preparation of BaFe$_{12}$O$_{19}$-coated glass fiber

The concentrated sulfuric acid and hydrofluoric acid were mixed in a volume ratio of 1:3 as a coursing solution. The glass fibers (diameter of 20μm) were immersed into the coursing solution for 3 minutes at 30°C~40°C under ultrasonic environment first, next washed with deionized water until the pH value of the washing water reached 7, and then washed with absolute ethyl alcohol 3 or 4 times or so before drying. After that, the cleaned glass fibers were immersed into the prefabricated sol for 5 minutes under ultrasonic environment. Then the glass fibers were pulled out smoothly, dried at 120°C, and heated at 500°C for 1h. The coating and drying process has been repeated for several times, and
finally the sample was placed in a box resistance furnace and heated at different temperatures to obtain barium ferrite film.

2.3. Performance testing

The coating state and the thickness of the barium ferrite film were observed by scanning electron microscope (SEM). According to the Chinese national military standard GJB2038A-2011, the attenuation efficiency of the samples was tested by the arch method, the test frequency was 2GHz-18 GHz, the incident angle was 8°, and the polarization direction was vertical polarization (VV). The mechanical properties of single fiber were examined using YG001A type electronic strength tester with tensile rate of 2mm/min.

3. Results and discussion

3.1. Effect of heat treatment temperature on tensile strength and film quality

As shown in Table 2, the film of samples exhibit a red-brown color when the heat treatment temperature was 600°C, with the increase of temperature, the sample color deepened, finally turned brown. In addition, SEM test results in Figure 1 showed that at 600°C of the heat treatment temperature, the barium ferrite grains on the sample surface developed imperfect, and the particle size was small. When the heat treatment temperature was 640°C, the development of barium ferrite crystal tend to be complete, showing a hexagonal lamellar morphology, and the particle size increased significantly. With further increasing the heat treatment temperature, the barium ferrite crystals in the film developed more complete, and the particle size continued to increase. When the heat treatment temperature was raised up to 720°C, the complete barium ferrite particles of hexagonal lamellar morphology, which is 1-2μm, can be observed. Therefore, with the increase of heat treatment temperature, the crystal particles of the sample gradually grew up, showing hexagonal lamellar morphology. This is due to the lower the heat treatment temperature, the less the solid phase reaction occurred (see formula (1)-(4)), and there were Fe₂O₃, BaFe₂O₄ and other intermediate phase in the product. With the rising heat treatment temperature, the solid phase reaction is complete, and the product becomes only barium ferrite.

\[
dry\ gel \rightarrow \gamma-Fe_2O_3 + BaCO_3 \quad (1) \\
\gamma-Fe_2O_3 + BaCO_3 \rightarrow BaFe_2O_4 + CO_2 \uparrow \quad (2) \\
\gamma-Fe_2O_3 \rightarrow \alpha-Fe_2O_3 \quad (3) \\
BaFe_2O_4 + 5\gamma-Fe_2O_3 \rightarrow BaFe_{12}O_{19} \quad (4)
\]

Table 2. Effect of heat treatment temperature on sample’s properties

| Heat treatment temperature(°C) | Color       | Film condition | Tensile strength(Mpa) |
|-------------------------------|-------------|----------------|-----------------------|
| 600                           | red-brown   | well-distributed | 1540                  |
| 640                           | brown       | well-distributed | 1078                  |
| 680                           | brown       | well-distributed | 484                   |
| 720                           | brown       | well-distributed | ——                   |
In addition, the test data from Table 2 showed that the heat treatment temperature had a significant influence on the tensile strength of BaFe$_{12}$O$_{19}$/ glass fiber. When the temperature was 600°C, the tensile strength of the sample was 1540 Mpa. With the rising heat treatment temperature, the tensile strength of the sample decreased rapidly, when the temperature was raised up to 680°C, the strength was only 484 Mpa, which could not meet the requirement of Chinese national military standard GJB 1872-94. When the temperature rose up to 720°C, embrittlement of the sample occurred.

3.2. Effect of heat treatment time on tensile strength and film quality

Figure 2 and Table 3 is the test result of the samples sintered for different time at 640°C. SEM test results showed that when the heat treatment time was 5min, particles in the film were mostly acicular morphology. With the extension of heat treatment time, the crystallinity of barium ferrite crystals increased, crystal growth tended to be complete and the particle size increased. When the heat treatment time was 30min, particles in the film showed significant lamellar morphology, and thereafter, with the extension of the heat treatment time, the lamellar morphology developed more perfect and the particle size was larger. In addition, it is showed in Table 3 that with the extension of heat treatment time, sample color gradually deepened, from red-brown to brown and finally converted into dark brown. This is due to the extension of solid phase reaction between intermediate phases, which is beneficial to the formation of the barium ferrite crystals and the growth of the grains when the heat treatment time is prolonged.

| Heat treatment time(min) | Color     | Film condition | Tensile strength(Mpa) |
|-------------------------|-----------|----------------|-----------------------|
| 5                       | red-brown | well-distributed | 1782                  |
| 15                      | brown     | well-distributed | 1298                  |
| 30                      | brown     | well-distributed | 1078                  |
| 45                      | brown     | well-distributed | 671                   |
| 60                      | dark brown| peel off       | 456                   |

The data in Table 3 also showed that with the extension of the heat treatment time, the strength loss of the sample increased. When the heat treatment time was 5min, the tensile strength of the sample was 1782 Mpa, while the heat treatment time was extended to 45min, the tensile strength dropped to
671 Mpa, still meet the GJB1872-94 requirements. When the sample was sintered for 1h at 640℃, the
tensile strength was only 456 Mpa, below requirement of GJB 1872-94 provisions, and the film peeled
off.

![SEM images of samples sintered for different time](image)

**Figure 2.** SEM images of samples sintered for different time (a.5min, b.15min, c.30min, d.45min,
e.60min)

The reason of the strength loss of the sample after heat treatment can be explained from two
aspects. On one hand, with the increase of heat treatment temperature, the thermal motion of particles
increases, the molecular bond is weakened, and the strength of the glass fiber decreases. On the other
hand, the surface of glass fiber is not smooth, but there are varying amounts of different sizes of
micro-cracks. Especially after HF roughening treatment, micro-cracks and defects in the glass fiber
surface are greatly increased. According to the Griffith's theory[10, 11], there is stress concentration
near the micro-cracks and defects in the surface of the glass fiber because of the thermal stress during
heat treatment. When the stress exceeds a certain critical value, cracks begin to expand and result in
the strength decrease of the glass fiber. The higher the heat treatment temperature, the longer the heat
treatment time, and the greater the stress of micro-cracks and defects, the more serious loss of the
strength the glass fiber would suffer.

3.3. Effect of coating times on attenuation efficiency

Figure 3(a) was the reflectivity curve of the prepared samples. Data showed that as the frequency
increases, the attenuation efficiency of the sample increased. When the frequency was 17GHz, the
attenuation efficiency of the sample was best. But in the 2GHz-18GHz range, the overall attenuation
efficiency of the sample was poor. Especially in the low frequency region, the attenuation efficiency
was only about 6%.

There are many factors influence the attenuation efficiency of absorbing materials, in addition to
the electromagnetic parameters and dimensions of the material itself, equalization of electromagnetic
parameters, surface roughness, cracks, and parallelism of the surface also have some effects. The low
attenuation efficiency of BaFe$_{12}$O$_{19}$-coated glass fiber prepared can be explained from the following
three aspects:

A. Due to the large surface tension of glass fiber, big difference between interfacial thermal
expansion coefficients and other factors, the film on the surface of the prepared material was rough
with inhomogeneous thickness and cracks, resulting in deterioration of the absorbing properties of the
material.

B. The distribution of absorbing agent in the sample was inhomogeneous, and the volume fraction
of electromagnetic wave transparent material was larger than that of the absorbing agent, so that the
power transmission coefficient of the material is larger, resulting in deterioration of the absorbing properties of the material.

C. The process of preparing thin films by sol-gel method is a process of non-equilibrium state and greatly influenced by the matrix, which is prone to abnormal crystal structure and microstructure, resulting in deterioration of the absorbing properties of the material. The main reasons are as follows: first, the lattice constant of the raw material does not match with the matrix material, in order to achieve the effective combination, crystal lattice distortion or crystal dislocation will occur near the interface between the film and the substrate. Second, because of the large curvature of the surface of glass fiber and its inconsistent thermal expansion coefficient with the film, the film is subjected to a large surface stress, resulting in the abnormal structure of the crystal.

![Figure 3. R-f curves of samples with different coating times (a.1, b.2, c.5, d.10)](image)

In summary, under single coating conditions, due to the rough, thin film of BaFe₁₂O₁₉-coated glass fiber and barium ferrite lattice distortion, the effective absorbing agent content of the sample was low, resulting in the limited attenuation efficiency. In order to improve the film quality and the effective barium ferrite content, the film quality and absorbing properties of multi-coating BaFe₁₂O₁₉-coated glass fiber samples were studied.

Data showed that, with the increase of coating times, the attenuation efficiency of the sample had been improved, and the absorption peak shift towards lower frequency. The bandwidth of reflectivity lower than -5dB of 2 times coated samples was 3.2GHz (Figure 3(b)), while 6.8GHz of 5 times coated samples (Figure 3(c)), 11.8GHz of 10 times coated samples (Figure 3(d)). In addition, as the frequency increases, the reflectivity of the sample significantly reduced, the attenuation efficiency significantly improved and was up to 60%-80% within 2GHz-18GHz, having a high practical value.

In summary, increasing the coating times of the film can improve the attenuation efficiency and broaden the absorption band of the sample. And with the increase of the coating times, the absorption peak shift towards lower frequency. SEM test results in Figure 4 showed that with the coating times
increased from 2 times to 10 times, the thickness of the barium ferrite film increased from 500nm to about 1.5μm. Therefore, increasing the coating times can increase the thickness of barium ferrite film and improve the surface state of the sample, which can improve the effective barium ferrite content and attenuation efficiency of the sample.

![Figure 4. SEM images of multiple coating samples (a.2, b.5, c.10)](image)

4. Conclusion

BaFe_{12}O_{19}-coated glass fiber composites prepared by sol-gel method have certain attenuation efficiency. Data show that the multi-coating samples have a best reflectivity of (15GHz, -6.65dB) and the bandwidth of reflectivity lower than -5dB is 11.8 GHz, having a high practical value. The increase of heat treatment temperature and time was in favor of barium ferrite grain growth, and will result in the loss of strength of the sample. Increasing the coating times can improve the film quality and attenuation efficiency of the sample.

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