Preparation and properties of magnesium oxysulfide inorganic microwave absorbing coating

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Abstract—This paper mainly introduces the harm of electromagnetic radiation pollution, and based on the electromagnetic wave absorption theory, the microwave absorption performance of single-layer microwave absorbing coating with magnesium oxysulfide cementitious material as matrix material and iron tailings as microwave absorbing agent is studied. The experimental results show that the absorbing effect of the absorbing coating mixed with 0.5 proportion iron tailings is the best, and the absorbing performance increases obviously with the increase of thickness. The maximum absorption value of 3mm thick coating sample is -6.0 dB. The prepared microwave absorbing coating has certain application value in electromagnetic protection.

1. Introduction
At present, radio technology has been widely used in many fields, covering a wide range, and achieved remarkable results. For example, the transmission of detection data in the aerospace field is inseparable from radio technology; Radar detection is indispensable in national defense and military affairs; In weather prediction, radio shows its unique discrimination performance. But the application of radio technology has also brought a negative impact on our life, which is electromagnetic radiation pollution, commonly known as invisible killer. Every corner of our living space is filled with electromagnetic radiation, which causes potential damage to our body. Based on the above background, it is necessary to protect electromagnetic radiation for our physical and mental health. In terms of electromagnetic protection, the first is microwave absorbing materials.
2. Important electromagnetic parameters of microwave absorbing materials

Microwave absorbing material refers to the material that can absorb the energy of incident electromagnetic wave and attenuate or eliminate this part of energy. Such materials either convert electromagnetic waves into heat or other forms of energy, or attenuate or eliminate them through resonance effect. Absorbing materials can fundamentally solve the problem of electromagnetic radiation pollution.

Absorbing materials are generally composed of matrix materials and absorbing media, which are usually related to the thickness of absorbing media, the content of absorbing media and the dielectric constant of dielectric layer.

The condition for electromagnetic wave absorption by materials is to meet the impedance matching characteristics and attenuation matching characteristics\(^\text{(1)}\), which must be considered in the design of microwave absorbing materials. We used to represent the internal electric induction intensity of the material, \(H\) to represent the magnetic induction intensity, and \(E\) to represent the electric field intensity. The relationship between them is:

\[
D = \varepsilon_i \varepsilon E, \quad B = \mu_i \mu H
\]

(1)

Where, complex permittivity \((\varepsilon)\) and complex permeability \((\mu)\) are two basic parameters of electromagnetic properties of absorbing materials, which are written in the complex form as follows:

\[
\varepsilon = \varepsilon' - j \varepsilon'', \quad \mu = \mu' - j \mu''
\]

(2)

Where: \(\varepsilon' / \mu'\) —polarization or magnetization of the absorbing material under the action of electromagnetic field;

\(\varepsilon''\) —Measurement of loss caused by rearrangement of electric dipole moment of material under applied electric field;

\(\mu''\) —Loss measurement caused by rearrangement of magnetic dipole moment of material under external magnetic field.

It can be seen that the ability of absorbing materials to absorb electromagnetic waves is mainly determined by the imaginary part \(\varepsilon''\) and \(\mu''\), and the dielectric loss angle \(\delta\) the tangent of is the loss factor, which is used to represent the size of dielectric loss. \(\tan \delta\) Can be expressed as:

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} + \frac{\mu''}{\mu'}
\]

(3)

Obviously, \(\tan \delta\) along with \(\varepsilon''\) and \(\mu''\) increase with increase, so the material \(\varepsilon''\) and \(\mu''\) the larger the, the better the absorbing property of the material.

3. Experimental instruments and equipment

The samples prepared in this experiment are all microwave absorbing coatings, and the microwave absorbing properties of single-layer and double-layer microwave absorbing coatings are actually tested. The specification (length, width and height) of each layer is 180 mm \(\times\) 180 mm \(\times\) 1 mm. The selected test equipment is av3629d microwave network vector analyzer, and the reflectivity measurement range is 2-18 GHz.

4. Properties of magnesium oxysulfide substrate

In the field of inorganic cementitious materials, magnesium cementitious materials are relatively mature and widely used. They have been widely used in municipal engineering, residential buildings, agricultural production and highway transportation. The main raw materials of the material are
magnesium chloride, magnesium oxide (or magnesium sulfate or magnesium phosphate) and water, which usually react to form a ternary cementitious system.

Magnesium cementitious materials mainly include magnesium oxychloride, magnesium oxysulfide and magnesium phosphate. The research of magnesium oxychloride cementitious material is relatively early and the technology is relatively mature. Because of its outstanding advantages such as green, environmental protection and energy saving, it has been widely used in the fields of architecture, building materials, decoration and so on. However, the application of magnesium oxychloride cementitious material is limited because it contains free chloride ions, which is easy to cause moisture absorption and halogen return. In contrast, magnesium phosphate cementitious material has the advantages of short setting time and high strength. However, the cost of magnesium phosphate cementitious material is relatively high, which is mainly used in engineering emergency repair, military industry and other fields.

The birth of magnesium oxysulfide material overcomes many disadvantages of magnesium oxychloride. The biggest advantage is that it does not absorb moisture, does not return halogen, and does not corrode reinforcement. Magnesium oxysulfide belongs to pneumatic cementitious material\(^\text{[1]}\), which is mainly prepared from magnesium oxide and magnesium sulfate. Its structure is $\text{MgO-MgSO}_4\cdot\text{H}_2\text{O}$ ternary cementitious system.

Magnesium oxysulfide cementitious material solves the problems of poor water resistance, easy deformation, easy moisture absorption and easy corrosion of reinforcement because there is no chloride ion in the raw material. At the same time, the material also has the characteristics of high temperature resistance, which makes it widely used in building materials and decorative materials.

When the temperature is high and the density of magnesium sulfate solution is high, the hardening speed of magnesium oxysulfide cementitious material is fast, so it is necessary to add retarder. In this experiment, citric acid was added as retarder.

Citric acid is one of the most widely used organic acids in the market. The chemical formula is \(\text{C}_6\text{H}_8\text{O}_7\), and the structural formula is shown in Figure 1. Citric acid usually contains a molecule of crystal water with strong sour taste and high solubility. It is a colorless, transparent or translucent crystal at room temperature. Citric acid can exist in the form of anhydrous or monohydrate and has slight deliquescence in humid environment. Due to strong acidity, citric acid has corrosive effect on carbon steel, but does not affect stainless steel. In case of strong oxidant, it can be oxidized to oxalic acid. Citric acid is widely distributed in orange, lemon and other plant fruits, as well as animal bones, muscles and blood. Synthetic citric acid is usually fermented from sugar and starch. At present, citric acid has been widely used as food additives, pharmaceutical coolants, pharmaceutical additives, metal cleaning agents, chromatographic analysis reagents, chromatographic analysis reagents, etc.

![Figure 1 Structural formula of citric acid](image)

The purpose of adding retarder is to prolong the hydration and hardening time of magnesium oxysulfide cementitious material, so that the cementitious material can maintain plasticity for a long time. After adding an appropriate amount of citric acid, the strength of magnesium oxysulfide cementitious material will be greatly improved \(^5\). Magnesium oxysulfide is an air hardening cementitious material. It has a very good degree of condensation and hardening in the air, which makes it have very good air stability. The drier the air is, the stronger the stability is. In a dry environment, the longer the time, the better the compressive strength of magnesium oxysulfide cementitious materials, and the weather resistance is unmatched by organic materials. However, magnesium oxysulfide cementitious material should not be used in humid environment or directly in water.
5. Properties of iron tailings
Iron tailings is a kind of industrial solid waste in China, which is usually the waste after beneficiation. Due to the beneficiation process, the content of metal compounds in iron tailings is relatively small, mostly non-metallic minerals or metal and non-metallic composite minerals. The types and contents of minerals contained in iron tailings will vary with iron ore types and distribution areas. However, most of the main minerals contained are quartz, pyroxene, feldspar, calcite, amphibole and so on. The main chemical components are oxides of iron, silicon, magnesium, calcium and aluminum, as well as a small amount of phosphorus and sulfur. The composition of iron tailings selected in this experiment is shown in Table 1.

| Chemical composition | MgO | Al₂O₃ | SiO₂ | K₂O | CaO | Fe₂O₃ | BaO | ZrO₂ |
|----------------------|-----|-------|------|-----|-----|-------|-----|------|
| Content (%)          | 2.41| 8.92  | 35.3 | 1.58| 3.23| 37.2  | 1.81| 6.63 |

Table 1 Main chemical composition of iron tailings (mass fraction%)

Figure 2 XRD spectrum of iron tailings
The shape of iron tailings is irregular, the particles are large and the distribution is uneven. During the experiment, the first thing to do is to fully grind the iron tailings and filter them with a sieve. After grinding and screening, its morphology and distribution will be significantly improved, which is conducive to the experiment. In this way, the prepared samples can achieve good microwave absorption effect. Figure 3-2 shows the scanning electron microscope of iron tailings. It can be seen from the figure that the shape of iron tailings is irregular, the particles are large and the distribution is uneven. During the experiment, the iron tailings should be fully ground to achieve good microwave absorption effect.

Figure 3 Microstructure of tailings

6. Effect of iron tailings on microwave absorbing properties of microwave absorbing coating
6.1. Coating sample preparation
Four samples with different tailings contents were prepared in this experiment. First, mix magnesium
oxide and magnesium sulfate in the proportion of 2:1, add an appropriate amount of citric acid and water, and stir for about 5 min. Due to the reaction of magnesium oxide, magnesium sulfate and water, the hardening is faster when the temperature is high and the density of magnesium sulfate solution is large, so an appropriate amount of citric acid needs to be added. However, too much citric acid should not be added. An appropriate amount of citric acid will strengthen the strength of the coating material, and excessive citric acid will weaken the strength. After the above materials are stirred evenly, add a certain proportion of tailings to continue mixing, then put them into the mold for molding and cure at room temperature for 24 hours. The coating samples are uniformly made, and the specification is 180mm × 180mm × 1mm size.

| Serial number | Mass ratio of magnesium oxide to magnesium sulfate | Proportion of tailings quality | Citric acid content (mass% MgO) |
|---------------|-----------------------------------------------|--------------------------------|---------------------------------|
| 1             | 2:1                                          | 0.0                            | 0.40%                           |
| 2             | 2:1                                          | 0.5                            | 0.40%                           |
| 3             | 2:1                                          | 1.0                            | 0.40%                           |
| 4             | 2:1                                          | 1.5                            | 0.40%                           |

In the process of sample preparation, special attention should be paid to the fluidity of the mixed slurry. The mold level must be ensured in the curing process, otherwise the uniformity of sample thickness will be affected. In the process of sample preparation, special attention should be paid to the fluidity of the mixed slurry. The mold level must be ensured in the curing process, otherwise the uniformity of sample thickness will be affected.

6.2. Coating sample test

![Effect of different tailings content on the performance of microwave absorbing coating](image)

It can be seen from Figure 4 that the reflectivity of the microwave absorbing coating sample without tailings is close to 0 in the range of 2-18 GHz, and basically does not have microwave absorbing characteristics. The microwave absorbing coating with 0.5 proportion of tailings reaches the maximum absorption value of -1.74 dB at 18 GHz; With the increase of tailings content, the absorption shows a downward trend. The maximum absorption value of the microwave absorbing coating mixed with 1.0 tailings is -1.03 dB at 18 GHz; The maximum absorption value of the microwave absorbing coating mixed with 1.5 proportion tailings is -0.34 dB at 18 GHz.

From the experimental results, it can be seen that the more tailings are added, the better the absorbing effect is. On the contrary, the absorbing effect becomes worse with the increase of tailings content. This is because too much tailings lead to the enhancement of interfacial reflection and poor microwave absorption effect of the composite.
7. Microwave absorbing properties of different thickness microwave absorbing coatings with the same tailings content

7.1. Coating sample preparation
Coating sample preparation in this part of the experiment, tailings with a proportion of 0.5 were selected to prepare three kinds of microwave absorbing coating samples, which are 1mm thick, 2mm thick and 3mm thick respectively. Similarly, the coating sample is uniformly made with a length and width of 180 mm × 180 mm size.

7.2. Coating sample test

![Graph showing reflection loss vs. frequency for different thicknesses.](image)

Figure 5  Effect of different thickness of the same tailings content on the properties of microwave absorbing coating

It can be seen from the test results that with the increase of thickness, the microwave absorption performance of the microwave absorbing coating is significantly improved. The maximum absorption value of the three samples reaches 18 GHz. The maximum absorption value of the 1mm thick coating sample is -1.74 dB, the 2mm thick coating sample is -4.07 dB, and the 3mm thick coating sample is -6.0 dB. The three samples have little difference in absorption effect in the range of 2-10 GHz, basically do not have microwave absorption performance, and there is obvious difference in absorption effect in the range of 10-18 GHz.

8. conclusion
It can be seen from the experimental results that the more the content of the absorbing agent is, the better the absorption effect is. When the content of the absorbing agent reaches a certain level, the absorption of the material to the electromagnetic wave gradually becomes worse with the continuous increase of the content. In addition, the thickness has a great influence on the microwave absorption performance of the coating. With the increase of the coating thickness, the maximum absorption capacity increases gradually. The innovation of this paper is to study the preparation of magnesium oxysulfide inorganic microwave absorbing coating. Compared with the traditional organic coating, the inorganic coating has no pollution to the environment, long service life, and has very good flame retardant, air permeability, antibacterial, alkali resistance and climate resistance. It is suitable for all mineral building materials. Magnesium oxysulfide cementitious material is one of many inorganic materials. It is selected as the base material because it has the advantages of easy crystallization, high strength, good water resistance and easy preparation of coating.
References

[1] Xing Yafei, Liu Cang, Liu Yinchao, et al. Analysis of noise spectrum and noise reduction effect of magnesium oxysulfide core lightweight sound insulation room [J]. Chinese Journal of labor health and occupational diseases, 2019,37 (8): 605-607

[2] Fu Xiyao. Research progress on the effects of modifiers and admixtures on the properties of magnesium oxysulfide cement-based materials [J]. Sichuan building materials, 2019,45 (9): 10-12

[3] He Nan, Hao Wanjun, Feng Fanian, et al. The absorbing properties of iron oxide and magnesia foam cement composite material. [J]. Journal of materials science and engineering, 2019,37 (3): 385-391.

[4] Chen Fangyu, Wu Chengyou. Study on properties of modified magnesium oxysulfide cement [J]. New building materials, 2018,45 (6): 56-58,62

[5] Zhang Xingfu, Wang Zifu, Wang Mingying, Jin Lutong, Liu Kun, Wang Yong. Study on modified magnesium oxysulfide composite wallboard [J]. New building materials, 2017,44 (06): 66-69

[6] Zhang Yuefang, Hao Wanjun. Research progress of microwave absorbing materials and its impact on military stealth technology [J]. New chemical materials

[7] Huang Yonggang. Utilization status and Prospect of iron tailings resources in China [J]. Resources and industry, 2013,15 (03): 40-44

[8] Zhu Huirong. Study on properties of magnesium oxysulfide cementitious materials [D]. Jilin Institute of architectural engineering, 2010

[9] Hao Wanjun, Zhao ran, Zhang Zhenhua, Zhang Fan, sun Changmeng, Chen Jianjian. Simulation calculation of high frequency electromagnetic radiation absorption characteristics of building walls [J]. Journal of environmental engineering, 2011,5 (07): 1671-1674

[10] Hou Jin, Chen Guohua. Effect of the amount of absorbing agent on the microwave absorbing properties of radar absorbing coating [J]. Materials guide, 2008,22 (S1): 314-315 + 320

[11] Jiang Lili, Liu Jiangwu, Dong Wenjun, Guo Jiata, Yu Siwen, Liu Bo, Yan Tingyi. Effect of citric acid content on water resistance of magnesium oxysulfide cement [J]. Silicate bulletin, 2016,35 (12): 4093-4096

[12] Zhao Lingzhi, Hu Shejun, Li Weishan, he Qinyu, Chen Junfang, Ru Qiang. Absorbing principle and research progress of absorbing materials [J]. Modern defense technology, 2007 (01): 27-31 + 48G. Eason, B. Noble, and I. N. Sneddon, “On certain integrals of Lipschitz-Hankel type involving products of Bessel functions,” Phil. Trans. Roy. Soc. London, vol. A247, pp. 529–551, April 1955.