Study on the decimeter wave absorbing materials

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Abstract. In order to confront the reconnaissance of decimeter wave radar, metal-oxide absorbing materials are studied according to the present development of decimeter wave absorbing materials. The decimeter wave absorption and temperature rising mechanisms of transition metal-oxide are analyzed, the wave absorption and temperature rising tests are conducted, and the temperature rising rates are compared. Testing results show some transition metal-oxides have good absorption of decimeter wave.

1. Introduction
The foreign radar reconnaissance technology has developed very rapidly, and the decimeter wave radar has been put into operation, and it is reported that the decimeter wave radar used by the U.S. military can penetrate leaves and sand at an altitude of 20 to 30km and find targets, with a penetration capacity of 8m for dry sand. In order to combat radar reconnaissance, it is necessary to develop high-efficiency radar wave absorbers. The present commonly used absorbers are carbonyl iron, carbonyl nickel, ferrite and other metal powder materials. However, the absorption peaks of these materials are mainly in the X, Ku and Ka bands, and the absorption performance in the L, S, C and other decimeter bands is pretty unsatisfactory[1-4]. It can be seen that for the use of more and more low-frequency radar reconnaissance equipment, it is necessary to carry out the research of low-band absorbent materials. And the key work is to develop new absorbent materials. In this study, it is proposed to break through the traditional absorption material style and develop an absorbent powder material of metal oxide series in order to fundamentally solve the problem of poor absorption performance in the low frequency band, which can lay a foundation for the development of coating-type absorbent material with good absorption performance in the low frequency band.

2. Microwave absorption mechanism

2.1. Absorbing mechanism
According to the viewpoint of quantum theory, the state parameters of microscopic system are quantized, that is to say, the parameters cannot take any value, and the values of parameters are discontinuous. For some reason, when the system transits from the state with energy E1 to another state with energy E2, if E1 is larger than E2, the system may radiate electromagnetic wave, and the frequency of the radiated electromagnetic wave is determined by the following formula [5]:

$$h \nu = E_1 - E_2$$  \hspace{1cm} (1)

On the contrary, if E2 is larger than E1, the system will absorb electromagnetic wave, and the frequency is determined by the following formula:

$$h \nu = E_2 - E_1$$  \hspace{1cm} (2)
It can be seen that the frequency of electromagnetic waves radiated and absorbed by the system cannot be arbitrary, it can only radiate or absorb electromagnetic waves of certain frequencies.

The corresponding quantum energy of decimeter wave (taking the microwave with a wavelength of 15 cm as an example) is \cite{5}:

\[ \varepsilon = h \nu = \frac{hc}{\lambda} = 1.33 \times 10^{-24} (J) \]  

(3)

This is the energy level interval of this material absorbing the microwave. This energy level gap is even smaller than the rotational energy level gap of common materials. This is the reason why effective decimeter wave absorbing materials have not been developed so far. The gap between conduction band energy levels of conductive materials is smaller than required here, which can be used to prepare absorbing materials, such as metal powder and carbon black. However, due to the high reflectivity of conductive materials and the skin effect of metals, the preparation of absorbing materials with pure conductive materials is limited. We must broaden our horizons. Using interface charge polarization and energy-stage division and quenching of orbital axon momentum under the action of crystal field, it is possible to obtain the required small energy-stage interval, which is the starting point of our study. Because the D-shell of transition group elements is dissatisfied, the d-electrons often participate in the chemical combination of metal and nonmetal, so the transition group elements often have different valence. They are multivalent elements, and the valence electrons have many different orbits with similar energy. Under the action of crystal field, these orbits further split, so we speculate that the energy level spacing of some transition group elements may be relatively small, and some compounds may have strong absorption to long wave (decimeter wave). In this paper, we try to make a preliminary comparative experimental study on the microwave absorption properties of transition group element oxides, and screen out the possible long wave absorption materials. Because of the high melting point and stable performance of metal oxides, transition metal oxides are used as the research object in this paper.

2.2. Temperature rising mechanism

The process of material absorbing electromagnetic radiation is related to the transformation of electromagnetic energy into other forms of energy. Therefore, the radiation intensity incident on the absorber is one of the basic factors that seriously affect the performance stability of the absorbing material. Irradiation time is another factor. The product of radiation intensity and irradiation time determines the energy per unit surface area of absorbent.

On the other hand, the thermal state of the absorbent also depends on the thermo physical properties of the absorbent. Thermal conductivity \( \lambda \) (w/m. K) and specific heat capacity C (J/kg. K) are the most important thermo physical parameters of materials. The density D (kg / m3) of absorbent material also affects the heating of objects. In addition, the convection process of heat exchange in solids can be ignored.

The change of temperature field in space and time can be described by parabolic equation, which is called thermal conductivity equation (in electrodynamics, wave equation is used for similar purposes). In general, the Cartesian coordinate system has the following form \cite{6}:

\[ cd \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right) + Q \]  

(4)

Here \( T = T(x, y, z, t) \) t is the temperature, t is the time, and \( Q = Q(x, y, z, t) \) is the function of the heat source, which determines the heat released per unit volume in unit time. In most cases, the thermo physical parameters, \( c \) and \( d \), can be considered temperature independent, and the solution of equation (2-4) has a fairly simple form. The thermal conductivity equation of the homogeneous material itself can be derived in the following form \cite{6}:

\[ \frac{\partial T}{\partial t} = a \nabla^2 T + Q/(cd) \]  

(5)
Here \( \alpha = \lambda/(cd) \) is the thermal conductivity, \( \text{m}^2/\text{s} \). For uniform absorbing materials, equation (4) can be written in the following form in one dimension \([6]\):

\[
\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + (1 - R) \frac{1}{cd} Q_0 e^{-\mu x}
\]

(6)

Where, \( Q_0 = \mu I_0 \), \( I_0 \) is the incident radiation intensity, \( \mu \) is the energy absorption coefficient and \( R \) is the energy reflection coefficient.

The single value of the solution of equations (4)-(6) depends on the form of the heat conduction equation and the known values of the corresponding initial conditions, boundary conditions and geometric conditions. The initial conditions determine the original temperature distribution, and the constant is usually assumed when calculating the heat of electromagnetic wave absorber. The boundary conditions determine the characteristics of the process on the surface of the object, and can be given in some ways. For example, the temperature distribution on the surface of the object may be given. Geometric conditions determine the shape and size of the object in the process of radiation. When arranging the boundary conditions, geometric conditions should be taken into account.

For a semi-infinite medium with no heat flux on the interface (or the non-timing can be ignored compared with the heat conduction process in the material, for example, when the electromagnetic wave absorber works in vacuum), the solution of equation (6) is as follows:

\[
T(x,t) = T_0 + \frac{2Q_0}{\lambda \mu} \sqrt{at} i \Phi^* \left( \frac{x}{2\sqrt{at}} \right) - \frac{Q_0}{\mu^2 \lambda} e^{-\mu x} \\
+ \frac{Q_0}{2\lambda \mu^2} \exp(\mu^2 - \mu x) \Phi^* \left( \mu \sqrt{at} - \frac{x}{2\sqrt{at}} \right) + \frac{Q_0}{2\lambda \mu^2} \exp(\mu^2 at + \mu x) \Phi^* \left( \mu \sqrt{at} + \frac{x}{2\sqrt{at}} \right)
\]

(7)

Where, \( \Phi(z) \) is the error function and \( i\Phi^*(z) \) is the integral of the error function.

\[
\Phi(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\xi^2} d\xi, \quad \Phi^*(z) = 1 - \Phi(z), \quad i\Phi^*(z) = \frac{1}{\sqrt{\pi}} e^{-z^2} - z\Phi^*(z)
\]

(8)

In the solution of equation (7), \( R = 0 \) is assumed. Therefore, it is correct only when the matching of electromagnetic wave absorbers is quite good. If the electromagnetic wave absorber has enough thickness, or has a large absorption coefficient \( \mu \), or works under the condition of short-term pulse, that is to say, it works under the condition that the temperature on the rear interface of the electromagnetic wave absorber does not have time to change significantly, the solution of equation (7) can be used.

Therefore, even in the simplest case, it is difficult to calculate the temperature state of electromagnetic wave absorber mathematically. In the case of absorber with arbitrary shape, this calculation is inconceivable without numerical method. In this sense, it is of great significance to study the thermal state of absorber by experimental method.

The heating process of object by microwave is closely related to the polarization of molecules. According to the types of micro particles involved in polarization, dielectric molecular polarization can be roughly divided into electron polarization, ion polarization, dipole steering polarization (orientation polarization) and interface polarization (also known as Maxwell Wapner polarization) \([7,8]\).

The relaxation time of the first two kinds of polarization is between \( 10^{-15}-10^{-16}\)s and \( 10^{-12}-10^{-13}\)s, while the vibration time of microwave alternating electric field is about \( 10^{-9}-10^{-12}\)s \([7]\). Therefore, the microwave field will not cause electron polarization and ion polarization, and the time range of some
dipole turning polarization and interface polarization just corresponds to the frequency range of microwave. The heating of medium in microwave field is mainly realized by these two polarization modes.

The polarization of dielectric in microwave field means the loss of electric field current density, and the complex permittivity of dielectric is \[ \varepsilon = \varepsilon' - i\varepsilon'' \] (9)

Where, \( \varepsilon' \) is the real part of the complex permittivity, which reflects the ability of the bound charge of the medium, and \( \varepsilon'' \) is the imaginary part of the complex permittivity, which reflects the loss of the medium and is often expressed by loss angle \( \tan\delta \):

\[ \tan\delta = \frac{\varepsilon''}{\varepsilon'} \] (10)

The complex permittivity \( \varepsilon \) comprehensively reflects the polarization behavior of dielectric in alternating electric field. In practical media, besides dipole loss \( \varepsilon_d'' \), there are interface loss \( \varepsilon_{MW}'' \) and conductivity loss \( \sigma / \omega \varepsilon_0 \). Therefore, the effective loss of the medium \( \varepsilon_{eff}'' \) (in the microwave field) is

\[ \varepsilon_{eff}'' = \varepsilon_d'' + \varepsilon_{MW}'' + \frac{\sigma}{\omega \varepsilon_0} \] (11)

Where \( \omega \) is the angular frequency of the microwave field, and the relationship between the loss factor and the frequency is shown in Figure 1. In the microwave frequency band, there are four main types: DC conductivity loss \( (c) \), relaxation loss of bound water \( (b) \), relaxation loss of free water \( (w) \), and interface loss \( (mw) \). The polarization loss of electrons and atoms exists in the infrared and visible parts of the electromagnetic spectrum.

The power lost by microwave in the process of heating medium, or the absorption of microwave frequency by medium, can be expressed as [7]:

\[ P = \omega \varepsilon_0 \varepsilon_{eff}'' E^2 \cdot V \] (12)

When a medium absorbs microwave energy, its temperature rise rate has the following relation:

\[ P = \frac{Q_h}{t} = \frac{M \cdot C_p (T - T_0)}{t} \] (13)

Using equation (12), the heating rate of the medium in the microwave field can be obtained as follows:
\[
\frac{(T - T_0)}{t} = \frac{0.566 \cdot 10^{-10} \cdot \varepsilon_\text{eff} \cdot f \cdot E^2}{\rho \cdot C_p}
\]  

(14)

Where, \( M \) is the mass of the medium, \( \rho \) is the density of the medium, \( C_p \) is the specific heat of the medium, and \( f \) is the microwave frequency.

If the microwave absorbing ability is strong, the heating rate must be high under microwave irradiation; otherwise, if the heating rate is high under microwave irradiation, the microwave absorbing ability must be strong. Therefore, we can study the heating characteristics of the materials as the basis for the primary selection of absorbing materials.

In addition, the quantitative relationship between the "peak" on the heating rate curve and the loss peak of the absorption spectrum is very complex, but there is an inherent correlation. The higher the temperature of the former, the lower the frequency of the latter. From this we can qualitatively infer the frequency loss.

3. Selection of experimental materials and equipment

Glantz wd800 household microwave oven is used as the main experimental equipment. Its input power is 1300W, output power is 800W and microwave frequency is 2450MHz. By measuring the temperature rise curve of transition metal oxides under microwave irradiation, the microwave absorption capacity of the materials at 2450MHz can be acquired.

The experiment was carried out in a completely closed environment, and the temperature was measured by thermocouple point thermometer (JT-1310). The temperature range was from -50°C to 1300°C. When the resolution is 0.1°C, the accuracy is ± (0.3% +1°C) in the range of -50°C ~ 199.9°C; when the resolution is 1°C, ± (0.3%+2°C) in the range of -50 ~ 1000°C. The specification of temperature measuring rod is TP-K01, and the contact is exposed bead. The wire of the temperature measuring rod is thin enough to be directly led out and clamped with the door of the oven, which has no effect on the power switch of the microwave oven.

4. Analysis of experimental results

The experimental data of each group are made into temperature-time curve, as shown in figure (2).

Fig.2 Calefactive curve of chemical

Enlarge the heating curve of several drugs whose heating is not obvious, as shown in figure (3).
It can be seen from the above two figures that except for the relatively monotonous heating curves of V2O5 and water, all other curves include two peaks, one trough and a constant temperature section which is basically parallel to the horizontal axis, and each peak and valley corresponds to one another. This shows that the heating trend of transition group element oxides under microwave irradiation is basically the same, but the heating rate and the time to reach the peak temperature are different. The order of the first peak is manganese dioxide - chromium trioxide - iron trioxide - titanium dioxide - nickel trioxide; the order of the second peak is manganese dioxide - chromium trioxide - titanium dioxide - nickel trioxide - iron trioxide. Manganese dioxide, nickel trioxide and vanadium pentoxide are the chemicals with faster temperature rise at room temperature.

The reason for the wave trough in the figure is estimated to be due to the different microwave radiation received by the left and right sides of the beaker during the heating process, resulting in different temperatures on both sides. More specifically, the right side continuously transfers heat to the left side. And when the temperature of the right side remains unchanged, the heat transferred to the left side decreases. But due to that the microwave oven keeps cooling, it will have the wave trough.

5. Conclusion
At present, the problem of long wave camouflage has not been solved. In this paper, we use experiments to explore the performance of transition group element oxides in absorbing decimeter wave, so as to lay a foundation for the further study of decimeter wave absorbing materials. From the experimental results, it can be seen that the transition group element oxides have a similar heating trend under decimeter wave irradiation, but the heating rate is obviously different, that is, the amount of absorbing wave is obviously different. It can be seen that MnO2, Ni2O3 and V2O5 have good microwave absorbing properties at low temperature, which can be used as the key research objects in the next step.

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