Journal of University of Science and Technology Beijing
Volume 11, Number 4, August 2004, Page 354

Materials

Heat radiative characteristics of ultra-attenuated materials

Dehong Xia and Yonghong Wu

Mechanical Engineering School, University of Science and Technology Beijing, Beijing 100083, China
(Received 2003-06-14)

Abstract: From the microstructure of heat radiation, the interaction between the incident heat radiative wave and the electromagnetism syntonic wave is analyzed to reveal the emission, absorption, transmission and reflection mechanisms of the incident heat radiative wave in materials. Based on Lorentz dispersion theory, the effect of optical parameters on heat radiative characteristics is also analyzed. The method of ultra-attenuation and nanocrystallization improving the heat radiative characteristics of the material and the emissivity dispersion of the ultra-attenuated materials are brought to light.

Key words: heat radiation; syntonic wave; dispersion; ultra-attenuation; nanocrystallization

1 Introduction

The heat radiative characteristics of materials mainly refer to those characteristics of absorbing, transmitting, reflecting and emitting the heat radiative wave. Heat radiative materials with unique heat radiative characteristics can make notable contribution to energy saving when applied in industry, daily life and national defence [1, 2]. A great deal of work on how to improve the heat radiative characteristics of different kinds of materials has been made all over the world. Ultra-attenuated materials behave quite different from ordinary materials in the fields of optics, electronics, magnetics, acoustics, mechanics, chemistry and biology [3]; they have unique heat radiative characteristics. It is proved practically that the metallic nano-grains are black and the reflectivity is lower than 1%. The intensive absorption results in the blackening of the metallic grains [4]. In fact, when a material is ultra-attenuated or nanocrystallized, the emissivity and absorptivity can be enhanced greatly. The research on ultra-attenuation will have a brilliant prospect.

2 Interaction between the heat radiative wave and the medium

The macroscopic heat radiative characteristics of materials reflect the state of the movement of particles including electrons and ions *etc.*, which changes with the outer electric field. As free electrons, bounded electrons and ions have different movement under the effect of the outer electric field, materials has different macroscopic heat radiative characteristics. **Figure 1** shows the interaction between the heat radiative wave and its projected medium. In this figure, all kinds of microscopic particles are vibratory periodically with micro-swing and certain inherent frequency. Under the effect of the outer heat radiative wave, the particles will be induced to move and their vibration states will be changed. Therefore, the macroscopic heat radiative characteristics of the material are presented on this occasion accordingly. But the interaction between the heat radiative wave and the particles in materials depends on the following conditions. Firstly, the wave caused by the vibration must be a transverse wave and its frequency and wave vector must match with the heat radiative wave. Secondly, the particles must form dipole moment under the effect of the heat radiative wave. Only these two conditions are fulfilled, the interaction between the incident heat radiative wave and the medium is most intensive and the absorption of the medium to the heat radiative wave is in larger percentage.

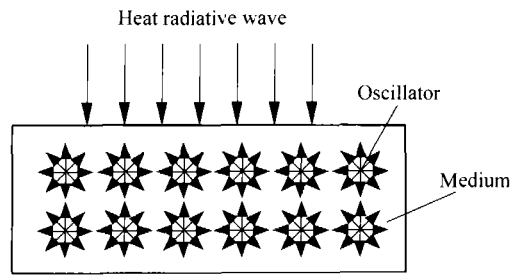

Figure 1 Interaction between the heat radiative wave and the medium.

2.1 Theoretical analysis on the transmitting of the heat radiative wave in the medium

When the heat radiative wave is transmitting in a

Corresponding author: Dehong Xia, **E-mail:** xia@me.ustb.edu.cn

medium, its wave vector $\vec{k}$ can be expressed by a complex wave vector [6]:

$$\vec{k} = \vec{k}_r + i\vec{k}_i \tag{1}$$

where the subscript r and i are the real part and the imaginary part of a complex number, respectively. So the electric field intensity $\vec{E}$ (or the magnetic field intensity $\vec{H}$) of the chromatic plane heat radiative wave with a turning frequency ω can be expressed as the relation of the space radius vector $\vec{r}$ and time t:

$$\vec{E} = \vec{E}_0 \exp(i\vec{k} \cdot \vec{r} - i\omega t) = \vec{E}_0 \exp(i\vec{k}_r \cdot \vec{r} - i\omega t)\exp(-\vec{k}_i \cdot \vec{r}) \tag{2}$$

Apparently, the swing of the electric field decreases with the imaginary part $\vec{k}_i$ and the radius vector $\vec{r}$ by way of exponent.

According to the Maxwell's equation group, the equation of wave vector $\vec{k}$ can be obtained:

$$\omega^2 \mu_0 \mu \varepsilon_0 \bar{\varepsilon} = \vec{k} \cdot \vec{k} \tag{3}$$

where $\bar{\varepsilon}$ and μ are the dielectric coefficient and magnetic susceptibility of the medium, respectively; ε_0 and μ_0 are the dielectric coefficient and magnetic susceptibility in vacuum, respectively. For the non-ferromagnetism medium, the magnetic susceptibility $\mu \approx 1$ and the light velocity in vacuum $c_0 = 1/\sqrt{\mu_0 \varepsilon_0}$, the formula above can be concluded as

$$\omega^2 \bar{\varepsilon} = c_0^2 (\vec{k} \cdot \vec{k}) \tag{4}$$

For the medium in which the swing of the heat radiative wave does not reduce, $\vec{k}$ is a real number and $\bar{\varepsilon}$ is a real number too. The following expression is obtained:

$$|\vec{k}| = k = \sqrt{\varepsilon}\omega / c_0 \tag{5}$$

For the medium in which the swing of the heat radiative wave reduces gradually, $\vec{k}$ is a complex number. Formula (4) can be expressed as

$$c_0^2 (|\vec{k}_r|^2 - |\vec{k}_i|^2 + 2i\vec{k}_r \cdot \vec{k}_i) = \omega^2 \bar{\varepsilon} \tag{6}$$

For the complex dielectric coefficient $\bar{\varepsilon} = \varepsilon_r + i\varepsilon_i$, the wave vector that satisfies formula (4) is also a complex number and all the resolutions to this equation are weakened wave. A comparatively simple circumstance is that $\vec{k}_r$ parallels to $\vec{k}_i$. Here formula (6) can be simplified as follows:

$$\begin{cases} c_0^2 (|\vec{k}_r|^2 - |\vec{k}_i|^2) = \omega^2 \varepsilon_r \\ c_0^2 (2\vec{k}_r \cdot \vec{k}_i) = \omega^2 \varepsilon_i \end{cases} \tag{7}$$

According to the definition of complex refractive index $\bar{n} = n + ik$, the real part is the refractive index n and the imaginary part is the extinction coefficient k. These two parameters and the complex wave vector have the following relation:

$$\begin{cases} n = |\vec{k}_r| \dfrac{c_0}{\omega} \\ k = |\vec{k}_i| \dfrac{c_0}{\omega} \end{cases} \tag{8}$$

So formula (7) can be simplified as follows:

$$\begin{cases} n^2 - k^2 = \varepsilon_r \\ 2nk = \varepsilon_i \end{cases} \tag{9}$$

The optical parameters n and k denote the heat radiative characteristics of materials. Other optical parameters relate with these two parameters.

2.2 Model of the interaction between the heat radiative wave and the medium

The optical parameters are not invariable, but change with the frequency of the incident heat radiative wave. Such dependence on frequency is called as dispersion. According to Lorentz dispersion theory [7, 8], the atom can be regarded as the harmonic oscillator constituted by atomic nucleus and electrons and ion can be regarded as the harmonic oscillator constituted by cation and anion on the basis of Newton mechanics. In order to simplify this model, the object studied in this paper is supposed to be uniform and isotropic. As a result, the interaction between the incident heat radiative wave and the material can be considered as the forced vibration of damping harmonic oscillators under the effect of the incident heat radiative wave. The damping constant γ shows the resistance resulted from the vibrating of the harmonic oscillators and it is supposed that there is only one type of harmonic oscillator of which the inherent frequency is ω_0 and the mass is m in the medium interacted with heat radiation. Considering a one-dimensional model, the coordinate x is the displacement of the harmonic oscillators under the effect of the incident heat radiative wave. The system of the harmonic oscillators is under the following forces: the elastic resilience $m\omega_0^2 x$ proportional to displacement x, damping force $-m\gamma \dfrac{dx}{dt}$ proportional to velocity and the drive force of the electric field $e^* E_0 \exp(-i\omega t)$, where ω and e^* are the frequency of the incident heat radiative wave and the effective electric charge of the harmonic oscillators, respectively. The damping constant γ which has the same dimension as the frequency indicates the collision frequency of the harmonic oscillators and it can be treated as a constant

which has nothing to do with the frequency. Under the effect of these forces, the movement function of a harmonic oscillator is expressed as follows:

$$m\frac{d^2x}{dt^2}+m\gamma\frac{dx}{dt}+m\omega_0^2x=e^*E_0\exp(-i\omega t) \tag{10}$$

Solving the above function, the displacement $x(\omega)$ of the harmonic oscillators under the effect of the heat radiative wave is concluded as

$$x(\omega)=\frac{e^*/m}{\omega_0^2-\omega^2-i\gamma\omega}E_0\exp(-i\omega t) \tag{11}$$

It is supposed that the number of the harmonic oscillators in a unit of volume is N. From the definition of the electric polarization intensity, it can be obtained that $\vec{P}=Ne^*\vec{x}=\varepsilon_0\chi\vec{E}$. So the complex polarizability is expressed as

$$\chi(\omega)=\frac{Ne^{*2}/m\varepsilon_0(\omega_0^2-\omega^2+i\gamma\omega)}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} \tag{12}$$

Ordering $\omega_p^2=Ne^{*2}/m\varepsilon_0$, the dispersion of the dielectric coefficient and the refractive index can be concluded as follows:

$$\varepsilon(\omega_r)=1+\chi_r(\omega)=1+\frac{\omega_p^2(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} \tag{13}$$

$$\varepsilon_i(\omega)=\chi_i(\omega)=\frac{\omega_p^2\gamma\omega}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2} \tag{14}$$

$$n^2(\omega)-k^2(\omega)=\varepsilon_r(\omega) \tag{15}$$

$$2n(\omega)k(\omega)=\varepsilon_i(\omega) \tag{16}$$

Here, the parameter ω_p, which is often called as the plasm frequency, is a characteristic frequency of materials. When the frequency of the incident heat radiative wave is higher than the plasm frequency, this material will show a transparent property.

From the above four formulas it can be concluded that the main factors that affect the optical parameters and the heat radiative characteristics of materials are the characteristic frequency ω_p, the inherent vibrating frequency (fundamental frequency) ω_0 of the harmonic oscillators and the damping constant γ. The parameter $\varepsilon_i(\omega)$, which has a close relation with the absorption is maximum when $\omega=\omega_0$. It decreases when the frequency is apart from ω_0 and tends to zero in higher and lower frequencies. This is a resonance effect. When the frequency of the incident heat radiative wave equals to the inherent frequency of the harmonic oscillators systems, the energy exchange between them is maximum and the systems absorb the incident heat radiative wave most intensively. If the harmonic oscillators vibrate in one inherent frequency, there is only one absorption peak. In fact, the harmonic oscillators may vibrate in different inherent frequencies, and then there are a lot of absorption peaks.

Though Lorentz dispersion theory adapts to isolator and semiconductor, it can be extended to apply in conductor and plasm. For the metal that has good conductivity, there are a great number of free electrons inside it and the bound force is 0, the inherent frequency of the electrons is also 0, namely $\omega_0=0$. Furthermore, the damping of the harmonic oscillators can be neglected for the plasm.

3 Heat radiative characteristics of ultra-attenuated materials

3.1 Effect of optical parameters on heat radiative characteristics of the materials

The surface radiative characteristics including the emissivity, absorptivity and reflectivity depend on the heat radiative property of a radiator, namely the refractive index and the extinction coefficient. According to the analysis of the surface radiative characteristics by electromagnetic theories, the normal chromatic reflectivity of general medium relative to the ideal dielectric is [10]:

$$\rho_{\lambda n}(\lambda)=\frac{(n-1)^2+k^2}{(n+1)^2+k^2} \tag{17}$$

From the formula above it can be concluded that the reflectivity equals to 0 if the refractive index n equals to 1 and the extinction coefficient k equals to 0. Furthermore, if $n=0$, $n\to\infty$ or $k\to\infty$, the reflectivity comes to the maximum 1. In order to reduce the reflectivity to increase the emissivity of the materials, the refraction to the incident heat radiative wave and the extinction coefficient of the materials should be decreased. The extinction coefficient is a physical parameter indicating the reducing speed of the incident heat radiative wave inside the materials. It represents the ability of the materials absorbing the heat radiative wave. The heat radiative wave reduces rapidly in the materials with high extinction coefficient. The materials intensively absorb the heat radiative wave and its transmission depth is very thin. By contrast, the incident heat radiative wave reduces slowly in the materials with low extinction coefficient. The transmission depth is very thick. Although the absorption ability of the materials with high extinction coefficient is strong, the heat incident radiative wave absorbed by the materials only includes those that penetrates through the surface of the materials, not includes the entire heat radiative wave. From formula (17) it can be concluded that the reflectivity of the materials with higher extinction coefficient is higher. Much of the

incident heat radiative wave is reflected by the surface of the materials and only a small fraction of the incident heat radiative wave can penetrate through the surface to enter into the interior of the materials. The emissivity and absorptivity of the materials with high extinction coefficient is rather low.

On the other hand, there are some relations between the refractive index and the extinction coefficient. According to Kramas-Krnig (KK) transform, the refractive index n equals to the integral of the extinction coefficient in a broad rang of frequency, and *vice versa*. When the extinction coefficient is low, the refractive index of the materials will approximately equal to 1 and the reflectivity will be low. If the extinction coefficient of the materials is 0, the materials could not absorb any heat radiative wave and the reflectivity of the materials definitely equals to 0. On this occasion the materials are transparent and can be penetrated by the heat radiative wave without reducing. It can be concluded that the absorption to the heat radiative wave is the premise of the reflection that depends on the absorption rate to the heat radiative wave.

3.2 Effect of ultra-attenuation on the heat radiative characteristics of the materials

Because of the small size effect, there are a great deal of crystal boundaries in ultra-attenuated and nanocrystallized materials and the movement of many microscopic particles including electrons and ions is confined to a range of the little grains. The smaller the size of the materials, the more disordered arrangement of the atoms in the crystal boundaries. On this occasion, the thickness of the crystal boundaries is increased and the scattering of the particles is enhanced. Based on the microscopic structure of ultra-attenuated materials, the scattering of the microscopic particles can be divided into two parts. The first part is the mutual scattering between the particles and the second part is the scattering that comes from the crystal boundaries. When the size of the materials is equivalent to the average free path of the electrons and ions, the scattering resulting from the crystal boundaries is dominant. On the other hand, when the size of the materials is much larger than the average free path of the particles, the scattering between the particles is of most importance. For ultra-attenuated materials, the effect of the crystal boundaries on the scattering is much greater than that of the inner particles. A great many crystal boundaries limit the movement of the microscopic particles greatly. With reduction of the size of the materials, the limitation is becoming greater and the resistance resulted from the movement of the electrons and ions increases gradually. Therefore the attenuation and nanocrystallization increase the resistance when the particles are moving.

Based on the approximation of Lorentz damping harmonic vibration above, the damping constant γ of ultra-attenuated materials is higher than normal materials because the harmonic oscillator constituted by the microscopic particles is under great resistance, which makes ultra-attenuated materials behave quite different from ordinary materials in the field of heat radiative characteristics. From formulae (13) and (14) it can be seen that if the plasm frequency is invariable, the real part and the imaginary part of the complex dielectric coefficient decrease continually with the increasing of the damping constant of harmonic oscillators. If the damping constant γ is close to infinite, the real part of the complex dielectric coefficient ε_r and refractive index tend to be 1, the imaginary part of the complex dielectric coefficient and extinction coefficient k tend to be 0. From the analysis above, it can be known that the emissivity of this kind of material is 1, which is a black body. This is enough to explain why ultra-attenuation can effectively improve the heat radiative characteristics of the materials to increase the emissivity and absorptivity of the material greatly.

To take the materials with the inherent frequency $\omega_0 = 3\times10^{14}$ Hz for example, when the plasm frequency $\omega_p = 10\times10^{14}$ Hz and the damping constants are assumed to be 1×10^{14}, 5×10^{14}, 10×10^{14} and 100×10^{14} Hz, respectively, the emissivity dispersion of the materials is shown in **figure 2** by the numerical calculations according to the formula about the emissivity in reference [11].

It can be concluded from figure 2 that the emissivity of normal block materials shows a strong dispersion because of the low damping constant. If $\omega_0 < \omega < \omega_p$, the emissivity and the absorptivity are minimum and the reflectivity is very high. The materials take on the characteristics of reflection. If $\omega \le \omega_0$, the emissivity is inversely proportional to the frequency of the incident heat radiative wave. If $\omega \ge \omega_p$, the emissivity is proportional to the frequency of the incident heat radiative wave. In the two frequency regions of $\omega \le \omega_0$ and $\omega \ge \omega_p$ the emissivity and absorptivity of the materials is much high, so the materials take on the characteristics of absorption. The emissivity dispersion of ultra-attenuated materials with high damping constant is not evident. It also can be concluded from the figure that the emissivity of ultra-attenuated materials is much higher than that of the normal ones and the emissivity is proportional to the damping constant and the frequency of the incident heat radiative wave. Reducing the size of the material to increase the damping constant would contribute to

enhancing the emissivity of the materials. But with the decreasing of the size of the materials and the increasing of the damping constant, the emissivity dispersion is becoming weaker and weaker. When the damping constant increases to a certain extend, the emissivity approximately equals to 1, which does not change with the damping constant and the frequency of the incident heat radiative wave. In other words, the emissivity is hard to improve and the materials can be treated as a black body when the size of the materials reduces to a certain extend.

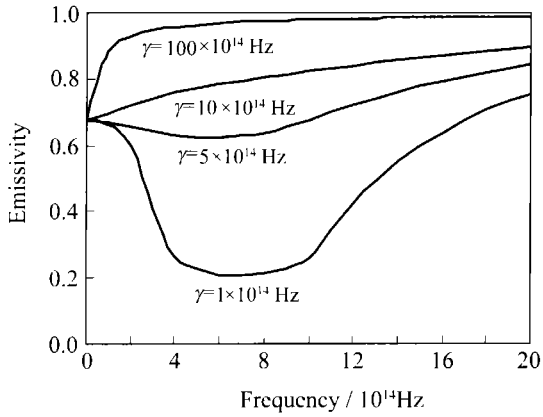

Figure 2 Emissivity dispersion of the materials.

It is noticeable that the depth of the materials is supposed to be larger than the transmission depth of the heat radiative wave on calculating the emissivity. The transmission of the heat radiative wave is neglected. In fact the depth of the materials will bring some effects on the emissivity of the materials, especially for the heat radiative wave with a large transmission depth. In addition, the effect of non-linear optics is also neglected in this paper because Lorentz dispersion theory is only applicable to linear optics. Finally though the plasm frequency depends on the size of the materials, its effect can be ignored when the damping constant is very high.

4 Conclusions

(1) The emission, absorption, transmission and reflection mechanisms of the incident heat radiative wave in materials are the interaction between the incident heat radiative wave and the electromagnetism syntonic wave in the projected materials.

(2) Based on Lorentz dispersion theory, the main factors that affect the optical parameters and the heat radiative characteristics of materials are plasm frequency, the inherent vibrating frequency of the harmonic oscillators and the damping constant.

(3) In order to reduce the reflectivity to increase the emissivity of materials, the refraction of the heat radiative wave and the extinction coefficient of the materials should be decreased.

(4) Because of the small size effect, the damping constant of ultra-attenuated materials is changed greatly, which makes ultra-attenuated materials behave quite different from ordinary materials in the field of heat radiative characteristics. Ultra-attenuation can increase the emissivity and absorptivity of the materials effectively.

(5) The emissivity dispersion of ultra-attenuated materials is not evident. When the microstructure size of the materials reduces to a certain extend, the emissivity does not change with the damping constant and the frequency of the incident heat radiative wave, which approximately equals to 1 and the materials behave as black bodies.

References

[1] J.G. Clements, High-Emissivity Coatings [J], *Heat Treat. Met.*, 13(1986), No.3, p.76.

[2] O.Y. Degang, T.S. Hu, A.Z. Luo, and X.J. Zhao, Study on radiant mechanism for high radiant materials [J], *Res. Iron Steel*, 2002, No.1, p.40.

[3] L.D. Zhang, J.M. Mou, *Nanomaterials and Nanostructure* [M], Science Press, Beijing, 2001, p.260.

[4] Y.R. Li and Z.Z. Yun, *Materials Physics Introduction* [M], Tsinghua University Press, Beijing, 2001, p.42.

[5] G.Y. Zhang, G.X. Lan, and Y.F. Wang, *Lattice Vibration Spectroscopy* [M], Higher Education Press, Beijing, 2001, p.112.

[6] J.N. Hodson, *Optical Absorption and Dispersion in Solids* [M], Chapman and Hall Ltd, London, 1970, p.10.

[7] H.A. Lorentz, *The Theory of Electrons* [M], Teubner, Leipzig, 1909, p.52.

[8] R.C. Fang, *Solid State Spectroscopy* [M], University of Science and Technology of China Press, Hefei, 2001, p.11.

[9] P. Jiang and Z.Z. Xu, *Solid Physics Concise Tutorial* [M], Fudan University Press, Shanghai, 2000, p.172.

[10] H.B. Sun, *Radiation heat transfer* [M], Metallurgy Industry Press, Beijing, 1996, p.93.

[11] P. Beckmann and A. Spizzichino, *The Scattering of Electromagnetic Waves from Rough Surfaces* [M], The Macmillan Company, New York, 1963, p.30.