ABSORPTION OF IR RADIATION AND THE OPTICAL FIELDS INSIDE METAL PARTICLES WITHIN OXIDE FILM

L.G. Astaf'eva and A.P. Prishivalko

Institute of Physics of the Academy of Sciences
of the Belorussian SSR, Minsk

Received June 19, 1989

The formation of an oxide film on the surface of an aluminum particle significantly changes the conditions of propagation of radiation inside such a two-layer particle, and this results in a significant increase of the relative fraction of the energy absorbed in it. For the range of particle sizes studied ($0.1 < R_2 < 20$ μm) even a not very large oxide shell, whose thickness comprises approximately 10% of the radius of the particle, increases the absorption of radiation by a factor of 15 compared with a metal particle of the same size.

It is well known that in air an oxide layer can form on the surface of metal particles. The thickness of the oxide film depends on the properties of the surrounding medium, the temperature, the pressure, etc.

It has been found experimentally[1] that under conditions of laser heating in air the absorptance of many metals changes. This happens because the laser radiation stimulates oxidation-reduction reactions on solid surfaces. The radiation induces oxidation of metals in air and the layer formed changes the absorptance of metal particles. Such processes are studied in laser macrokinetics.[2–4] Thus detailed study of metal particles with an oxide film is an important problem.

The optical properties of unoxidized metal particles have been studied previously.[5,6] Analogous studied of the optical properties of metal particles with an oxide film have not yet been performed.

The optical properties of an oxidizing metal particle can be described, to a first approximation, with the help of the model of a two-layer spherical particle consisting of a metal core and a shell consisting of the oxide of the metal. In this paper the absorption of such two-layer particles is evaluated and the optical fields inside them are studied as a function of the particle radius and the thickness of the oxide film. The study is performed for the example of particles of aluminum and radiation wavelength $\lambda = 10.6$ μm. The optical constants of aluminum and aluminum oxide are $m = 34.2 - i109$ (Ref. 7) and $m = 0.52 - i0,063$ (Ref. 8), respectively.

Figure 1 shows the dependence of the absorption efficiency factors of uniform particles of aluminum and aluminum- oxide as well as two-layer particles with an aluminum core and an Al_2O_3 shell as a function of the outer radius of the particle R_2. Each line was constructed with a constant ratio of the core radius R_1 to the outer radius of the two-layer particle R_2. For $R_1/R_2 = 1$ (no oxide shell) we have a uniform particle of aluminum; in the other extreme case $R_1/R_2 = 0$ we have a uniform particle of aluminum oxide. Intermediate values of the ratio $0 < R_1/R_2 < 1$ characterize two-layer particles with an oxide film.

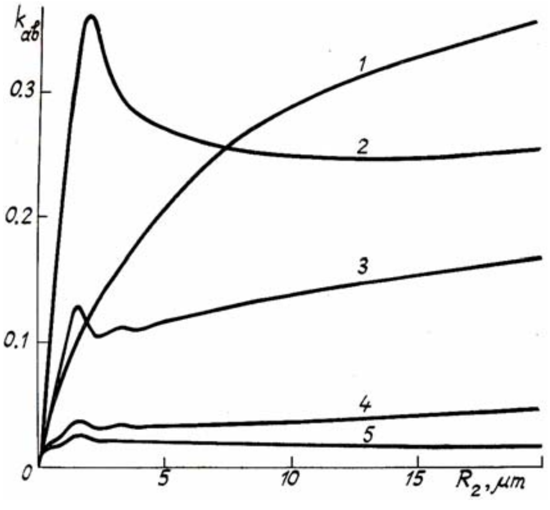

FIG. 1. Curves of the absorption efficiency of two-layer particles versus the outer radius of the particles. The numbers on the curves indicate the values of the ratio R_1/R_2: 1) 0, 2) 0.9, 3) 0.99, 4) 0.999, and 5) 1.

For values of the particle radii in the range $0 < R_2 \le 20$ μm the efficiency of absorption of radiation by a uniform particle of aluminum is low ($k_a \le 0,026$); this is explained by the strong reflection of radiation from metal surfaces. As regards the absorption by uniform particles of aluminum oxide, in this interval of particle radii the efficiency of absorption of radiation by Al_2O_3 particles increases monotonically as their size increases. As one can see from Fig. 1, in the interval $0 \le R_2 \le 20$ μm the absorption efficiency of Al_2O_3 particles is significantly higher than that of uniform particles of aluminum with the same radius (for $R_2 \ge 10$ μm 17 and more times higher).

As the two-layer particle becomes larger its absorption efficiency at first increases rapidly, reaches a maximum, and then decreases. In addition, for $R_1/R_2 = 0.999$ and $R_1/R_2 = 0.99$ as R_2 increases further the absorption efficiency starts to increase almost immediately. In the case $R_1/R_2 = 0.9$ k_a decreases in the range $2 < R_2 < 15$ μm and only then increases somewhat.

Thus the presence of an oxide layer on the surface of an aluminum particle results in a rapid increase of the absorption of radiation compared with a uniform particle of aluminum of the same size. For example, even a thin oxide shell, whose thickness is equal to about 1% of the radius of the particle ($R_1 = 9.9$ μm and $R_2 = 10$ μm), increases the absorption of radiation at the given wavelength by a factor of 8, while an oxide film whose thickness is equal to about 10% of the radius ($R_1 = 9$ μm, $R_2 = 10$ μm) increases the absorption by a factor of 15. In the range $0.5 < R_2 < 7$ μm the absorptance of two-layer particles is significantly higher than that of particles of aluminum oxide of the same size.

In the same range of particle sizes increasing the thickness, of the oxide film at first increases the absorption by the two-layer particle, and then for some thickness of the oxide layer the absorption efficiency starts to decrease. This is apparently caused by the fact that in not very thick shells of two-layer particles the incident light and the light reflected from the metal core are absorbed. In the case of thicker shells the effect of the core is weaker. For $R_2 > 8$ μm an increase in the thickness of the oxide film is accompanied by an increase in the absorption by the two-layer particle.

The above-studied change brought about by the formation of oxide films on aluminum particles in the absorption of the aluminum particles is connected with the distribution of energy inside such particles. We investigated the distribution of energy inside aluminum particles, which is also characteristic for other metals, in Ref. 9. The absorbed energy is concentrated in a thin layer near the surface of the particle. The energy density decreases rapidly away from the surface of the particle toward its center; it decreases by a factor of e on a layer whose thickness is of the order of 0.1% of the radius of the particle. The energy density is maximum in the illuminated hemisphere on the surface of the particle with $\theta = 0°$, i.e., at the end of the so-called principal diameter closest to the source.

The character of the distribution of the energy density inside the aluminum core of a two-layer particle with an oxide film is analogous to the energy distribution in a uniform aluminum particle. The energy is maximum in the illuminated hemisphere on the principal diameter on the surface of the core, but it is somewhat lower than in a uniform aluminum particle of the same size. In the shadow hemisphere the highest energy density is also found on the surface of the core, and it is also somewhat lower than the corresponding energy density in an aluminum particle. The maximum energy density in the core depends on the thickness of the oxide shell and decreases as the thickness decreases. This is connected with the fact that as the thickness of the shell increases an increasingly larger fraction of the energy incident on the particle is released in the shell and an increasingly smaller fraction of the energy is reflected from the boundary of the core.

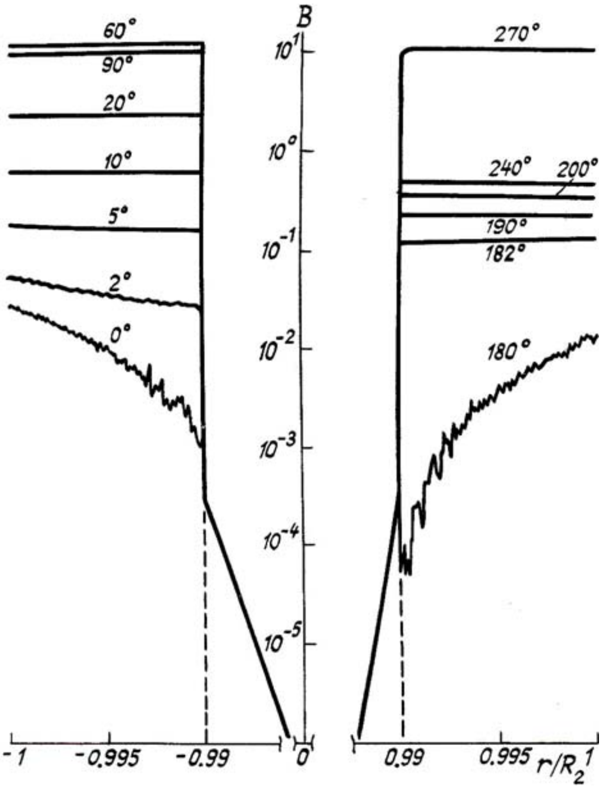

FIG. 2. The distribution of the relative energy density of the electric field B inside a two-layer particle with $R_1 = 9.9$ μm and $R_2 = 10$ μm. The numbers on the curves are the values of the angle θ. The dashed lines correspond to the boundary between the core and the shell.

The energy distribution in the aluminum oxide shell is completely different. To some extent it is similar to the energy distribution in a uniform aluminum oxide particle, but there is a difference. In particular, the maximum values of the energy density, like in a uniform Al_2O_3 particle, are observed not on the principal diameter of the particle but rather in the range of angles 30÷80°. Figure 2 shows a picture of the distribution of the energy density of the electric field, characterized by the ratio $B = \frac{\vec{E} \cdot \vec{E}^*}{|\vec{E}_0|^2}$ ($\vec{E}_0$ and $\vec{E}$ are the electra field intensities in a plane electromagnetic wave incident on the particle and inside the particle)^{10} inside a two-layer particle with an aluminum core and an oxide film. For a two-layer spherical particle with $R_1 = 9.9$ μm and $R_2 = 10$ μm the maximum energy density is $B = 13.7$ and is found at θ ≈ 73° in the shell near the shell-core boundary. It should be noted that the graphs of the energy distribution in the shell along the directions $0 \le \theta < |\pm 5°|$ and $175° < \theta < 185°$ oscillate strongly. This is evidently connected with the interference of the incident and reflected light in the particle shell, since the metal core strongly reflects the radiation incident on it. For $\theta > 5°$ the dependence $B(r)$ practically does not oscillate, while the value of B increases insignificantly from the surface of the two-layer particle to the core and reaches a maximum, as already mentioned, near the core shell boundary. This tendency is stronger as the radius of the core of a two-layer particle decreases. The value of $B_{\max}$ is higher in particles with a thinner oxide shell. In addition, the angle at which $B_{\max}$ occurs also becomes larger. For example, for particles with an outer radius R_2 = 20 μm and a core radius R_1 = 19 μm $B_{\max} \approx 0.7$ ($\theta \approx 52°$) and for R_2 = 20 μm and R_1 = 19.8 μm $B_{\max} \approx 11$ ($\theta \approx 62°$). It should also be noted that for the direction θ = 90° the energy density is quite high compared with the analogous direction in a uniform Al_2O_3 particle.

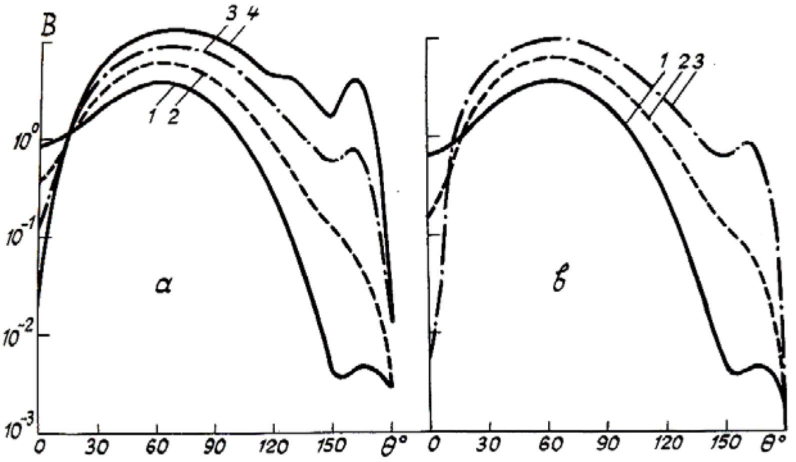

FIG. 3. The distribution of the relative energy density of the electric field B over the surface of the particle (a) and at r = 9.8 μm (b) inside the oxide shell of two-layer particles with different radii of the core R_1 = 9 (1), 9.5 (2), 9.75 (3), and 9.9 (4) μm and a constant outer radius R_2 = 10 μm.

Consider the energy distribution over the surface of the particle and in the oxide layer near the surface as a function of the angle θ (Fig. 3). The energy density is maximum for angles in the range $50° < \theta < 80°$ and on the surface and in the layer near the surface. The thinner is the oxide film on the surface of the aluminum core, the higher is the maximum energy density in the shell of the two-layer particle.

Thus the appearance of even a thin oxide film on the surface of a metal particle results in a significant change in the distribution of the energy inside the particle and to a corresponding significant increase of the absorption of the incident radiation. Analogous results were obtained in calculations of the absorption and distribution of energy inside particles consisting of other metals particles with an oxide film.

REFERENCES

1. M.I. Arzuov, V.I Konov, V.V. Kostin, S.M. Metev, A.S. Silenok, and N.I. Chapliev, *Investigstion of the Genetics of the Heating of Metals in a gaseous medium by continuous-wave and periodic-pulse CO_2 laser radiation,* Preprint No. 152, Institute of Physics of the Academy Sciences of the USSR, Moscow (1977).

2. F.V. Bunkin, N.A. Kirichenko, and B.S. Lukyanchuk, Usp. Fiz. Nauk, **138**, No. 1, 45 (1982).

3. F.V. Bunkin, N.A. Kirichenko, and B.S. Lukyanchuk, Vest, Akad. Nauk SSSR, No. 12, 58 (1987).

4. V.A. Besprozvannykh, V.A. Ermakov, and A.A. Razdobreev in: *Proc. of the Eighth All-Union Conference on Conbustion and Explosion,* Tashkent, October 13–17, 1986, Chernogilovka, 58 (1986).

5. C. Bohren and D. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, N.Y. [in Russian, Mir, Moscow (1986)].

6. N.N. Belov, Ukr. Fiz. Zh., **33**, No. 6, 831(1988).

7. M.A. Ordal, L.L. Long, R.J. Bell, S.E. Bell, R.R. Bell, R.W. Alexander and C.A. Ward, Appl. Opt. **22**, No. 7, 1099 (1983).

8. U.K. Lingart, V.A. Petrov, and N.A. Tikhonova, Teplofiz. Vys. Temp. **20**, No. 6, 1085 (1982).

9. L.G. Astaf'eva, A.P. Prishivalko, and S.T. Leiko, Fiz. Khim. Obrab. Mater., No. 4, 35 (1989).

10. A.P. Prishivalko, *Optical and Thermal Fields Inside Light-Scattering Particles* (Nauka i Tekhnika, Minsk, 1983).