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Emissivity of Al_2O_3 Particles in a Rocket Plume

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The infrared radiance from the plume of an aluminized rocket is anomalously high; however, the responsible physical mechanism is not known. In this paper, the conclusion is reached that the high emissivity is most likely due to the Al_2O_3 particulates containing very small amounts of aluminum and/or carbon impurities. To support this conclusion, experimental results of the radiance from single-alumina particles are discussed and calculated emissivity spectra of microscopic composite particles of alumina-carbon and alumina-aluminum are presented.

Introduction

THE understanding of the infrared radiative properties of micron-sized particles present in rocket plumes is fraught with uncertainties. This is demonstrated by considering the thermal emittance observed from the plume of an aluminized solid-propellant rocket whose exhaust consists of a number of gases and Al_2O_3 particles.[1] The observed radiance, which is known to be due mainly to the alumina, is high; yet, bulk samples of Al_2O_3 have very small extinction coefficients in the infrared, which implies low emissivities for particles. In fact, in the spectral range 2000-5000 cm^{-1} (5-2 μm), the micron-sized particle emissivity, calculated using the Lorenz-Mie theory[2] and bulk refractive index values, is orders of magnitude lower than that inferred from the plume emittance.

The physical mechanism responsible for this discrepancy is not known, due primarily to lack of particle experimental data. Recently, Rieger[3] suggested that the anomalous emission might be due to the Al_2O_3 particles containing impurities of metallic aluminum. In this paper, we discuss the results of emittance measurements performed on single-alumina particles. Motivated by these results, we present theoretical calculations of particle emissivity for a simple contamination model. We expand on metallic aluminum impurities as the source of enhanced emissivity, and reach a conclusion with regard to the observed high emittance from rocket plumes.

Experimental Results

We are presently measuring the thermal emittance from laser-heated, single, spherical particles of micron size to deduce the particle emissivity.[4] We have found that when an Al_2O_3 particle is irradiated with a focused cw CO_2 laser beam, its emissivity starts out anomalously high, but a short time later drops to a low value. Such anomalous emissive behavior raised questions as to the purity of the samples. For this reason, an analysis of the chemical composition of the surface of the Al_2O_3 particles was carried out using Auger electron microscopy.[5]

Figure 1 shows a superposition of the Auger spectra of two different alumina particles where a 3-kV incident electron beam was used; both spectra show peaks at the same Auger electron energies. The peaks at $\approx$68 and $\approx$1396 eV are from aluminum, while the peak at $\approx$503 eV is from oxygen. A fourth peak occurs at $\approx$272 eV and is due to the presence of carbon. Thus we find that our alumina, obtained from two different sources, are contaminated with carbon. Other investigators working with bulk samples of Al_2O_3 have also encountered similar carbon contamination problems.[6,7]

The question remains as to how the carbon is distributed in the particle. In Auger analysis, information in the form of Auger electrons can originate anywhere in a region extending from the surface down to $\approx$0.002 μm. The escape depth of a given Auger electron depends on its energy. The escape depth of the low-energy Al electrons (68 eV) is $\approx$0.0004 μm, while the escape depth of the high-energy Al electrons (1396 eV) is $\approx$0.0015 μm.[5] This means that if a contaminant such as carbon exists as a thin film on the surface of the alumina, it will attenuate the Al low-energy electrons more strongly than the high-energy electrons. Thus, for a suitably thin film of carbon on the surface of the alumina particle, a variation in film thickness can have a large effect on the 68-eV peak of the Auger spectrum while leaving the 1396-eV peak virtually unchanged. Returning to Fig. 1, we see that this is exactly what is observed; in the upper and lower spectra, the 1396 eV Al peaks are approximately the same size, while the 272 eV carbon peaks are quite different, indicating a thicker carbon film in the lower spectrum. Note the corresponding decrease in the 68 eV Al peak. Hence, the Auger spectra indicate that the carbon contamination is at least partly in the form of a surface film. The analysis shows the film thickness to vary from particle to particle; we estimate this surface carbon-containing contaminant to be on the order of 0.001-0.002 μm.

Theoretical Formalism

To confirm if, indeed, such a thin layer of a contaminant can drastically change the optical properties of micron-sized particles, the theory of Aden and Kerker,[8] which is an extension of the Lorenz-Mie theory, is used to solve for the interaction of electromagnetic radiation with a sphere coated with a layer of a different material. We have extended the application by considering materials for the inner sphere and the outer coating with complex index of refraction. The geometry and the different constants are depicted in Fig. 2. The far-field solution is obtained by requiring that the tangential components of the electric field and magnetic field vectors be continuous across the particle boundaries; the theory is fully derived and explained in Ref. 9. For ease of reference, the pertinent equations are presented here.

The amount of energy removed from an incident beam by the composite particle, just as in the Lorenz-Mie theory, is represented by the extinction cross section

$$\sigma_{ext} = \frac{\lambda^2}{2\pi} \sum_{n=1}^{\infty} (2n+1)\{Re(a_n + b_n)\} \tag{1}$$

The total power scattered by the particle is given by the scattering cross section

$$\sigma_{sca} = \frac{\lambda^2}{2\pi} \sum_{n=1}^{\infty} (2n+1)\{|a_n|^2 + |b_n|^2\} \tag{2}$$

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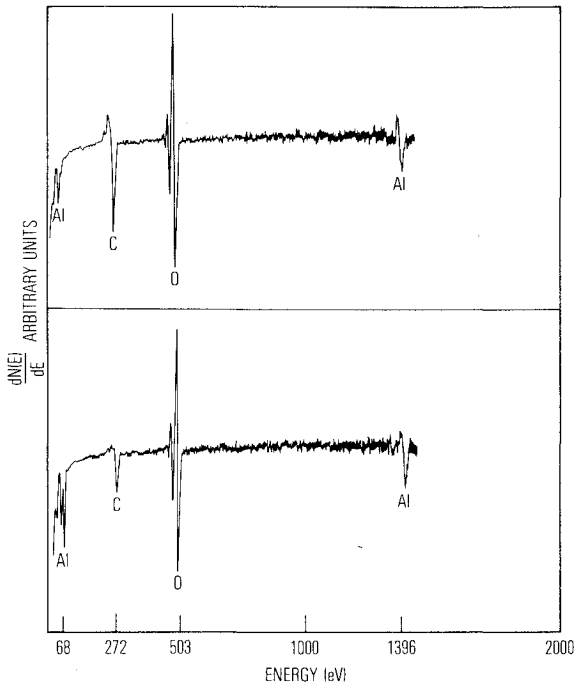

Fig. 1 Derivative Auger spectra of two different Al_2O_3 particles.

and, using the law of conservation of energy, the amount of energy removed from the incident beam, less the amount scattered, gives the cross section for the power absorbed.

The a_n and b_n are the electric and magnetic multipole coefficients, expressed in terms of the complex indices of refraction of the two materials, $\hat{n}_1$ and $\hat{n}_2$, and the size parameters for the sphere, $\alpha = 2\pi r_1/\lambda$, and the sphere plus shell, $\nu = 2\pi r_2/\lambda$.

$$a_n = \frac{\begin{vmatrix} \psi_n'(\hat{n}_2\alpha) & \chi_n'(\hat{n}_2\alpha) & \psi_n'(\hat{n}_1\alpha) & 0 \\ \hat{n}_2\psi_n(\hat{n}_2\alpha) & \hat{n}_2\chi_n(n_2\alpha) & \hat{n}_1\psi_n(\hat{n}_1\alpha) & 0 \\ \psi_n'(\hat{n}_2\nu) & \chi_n'(\hat{n}_2\nu) & 0 & \psi_n'(\nu) \\ \hat{n}_2\psi_n(\hat{n}_2\nu) & \hat{n}_2\chi_n(\hat{n}_2\nu) & 0 & \psi_n(\nu) \end{vmatrix}}{\begin{vmatrix} \psi_n'(\hat{n}_2\alpha) & \chi_n'(\hat{n}_2\alpha) & \psi_n'(\hat{n}_1\alpha) & 0 \\ \hat{n}_2\psi_n(\hat{n}_2\alpha) & \hat{n}_2\chi_n(\hat{n}_2\alpha) & \hat{n}_1\psi_n(\hat{n}_1\alpha) & 0 \\ \psi_n'(\hat{n}_2\nu) & \chi_n'(\hat{n}_2\nu) & 0 & \zeta_n'(\nu) \\ \hat{n}_2\psi_n(\hat{n}_2\nu) & \hat{n}_2\chi_n(\hat{n}_2\nu) & 0 & \zeta_n(\nu) \end{vmatrix}} \tag{3}$$

$$b_n = \frac{\begin{vmatrix} \hat{n}_2\psi_n'(\hat{n}_2\alpha) & \hat{n}_2\chi_n'(\hat{n}_2\alpha) & \hat{n}_1\psi_n'(\hat{n}_1\alpha) & 0 \\ \psi_n(\hat{n}_2\alpha) & \chi_n(\hat{n}_2\alpha) & \psi_n(\hat{n}_1\alpha) & 0 \\ \hat{n}_2\psi_n'(\hat{n}_2\nu) & \hat{n}_2\chi_n'(\hat{n}_2\nu) & 0 & \psi_n'(\nu) \\ \psi_n(\hat{n}_2\nu) & \chi_n(\hat{n}_2\nu) & 0 & \psi_n(\nu) \end{vmatrix}}{\begin{vmatrix} \hat{n}_2\psi_n'(\hat{n}_2\alpha) & \hat{n}_2\chi_n'(\hat{n}_2\alpha) & \hat{n}_1\psi_n'(\hat{n}_1\alpha) & 0 \\ \psi_n(\hat{n}_2\alpha) & \chi_n(\hat{n}_2\alpha) & \psi_n(\hat{n}_1\alpha) & 0 \\ \hat{n}_2\psi_n'(\hat{n}_2\nu) & \hat{n}_2\chi_n'(\hat{n}_2\nu) & 0 & \zeta_n'(\nu) \\ \psi_n(\hat{n}_2\nu) & \chi_n(\hat{n}_2\nu) & 0 & \zeta_n(\nu) \end{vmatrix}} \tag{4}$$

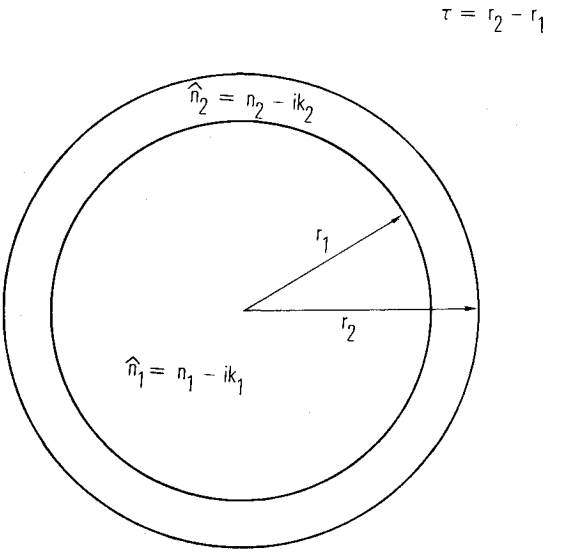

Fig. 2 Geometry and parameters used in the calculations for a sphere coated with a spherical shell.

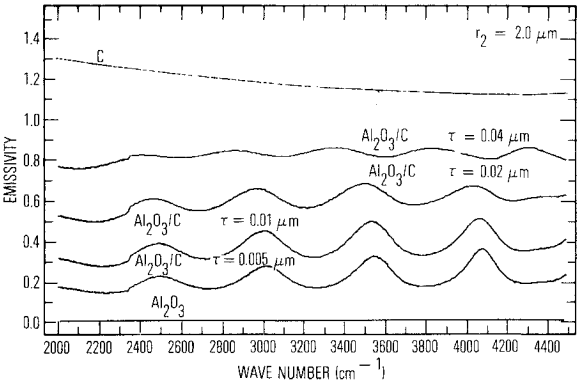

Fig. 3 Emissivity spectra for Al_2O_3, bottom spectrum, and carbon-coated Al_2O_3 particles with carbon layer thickness $\tau = 0.005$, 0.01, 0.02, and 0.04 μm. Top spectrum is for a pure carbon particle.

where ψ, χ, and ζ are the Riccati-Bessel functions. Obviously, the larger the particle the higher the order of multipoles that have to be included in the series above.

To obtain the expression for the particle emissivity, Kirchhoff's law is used to equate the power radiated to the power absorbed. The emissivity[10,11] is then given by

$$\epsilon = \sigma_{abs}/\pi r_2^2 \tag{5}$$

that is, the ratio of absorption and geometric cross sections.

For brevity, the results presented below will be discussed only as they pertain to the problem under consideration; particle optical behavior manifest in some of the emissivity spectra and the insight that can be obtained will be presented elsewhere.

Numerical Results

Emissivity spectra for an Al_2O_3 and a carbon-coated Al_2O_3 particle were calculated using refractive index values given in Ref. 12. The results are presented in Fig. 3 for a particle with overall radius remaining fixed at 2.0 μm. In this and following figures, the abscissa is wavenumber in units of reciprocal centimeters. The bottom curve is for a particle consisting of pure Al_2O_3; the emissivity is less than 10^{-3} throughout the

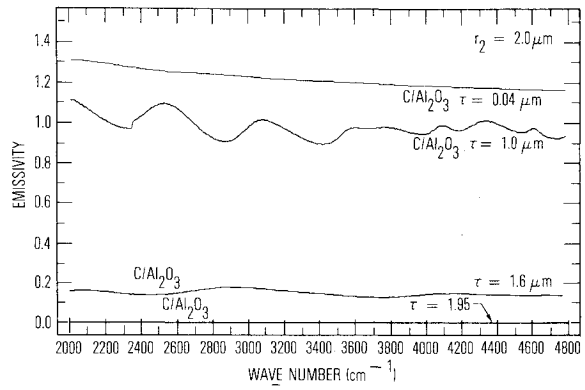

Fig. 4 Emissivity spectra of carbon-alumina composite particles with varying alumina layer $\tau = 0.04$, 1.0, 1.6, and 1.95 μm.

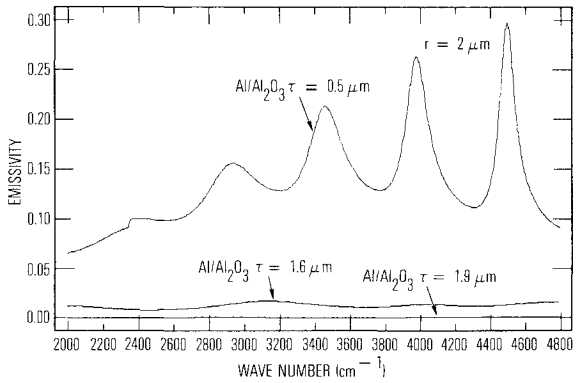

Fig. 5 Emissivity spectra of aluminum-alumina composite particles with varying alumina layer $\tau = 0.5$, 1.6, and 1.9 μm.

frequency range. However, by substituting the 0.005 μm nearest to the surface with carbon, the emissivity increases by approximately three orders of magnitude. It continues to increase as the carbon thickness is increased to $\tau = 0.01$, 0.02, and 0.04 μm. For comparison, the emissivity spectrum for a pure carbon particle of the same size, labeled C, is included in this figure.

These calculated results confirm our experimental observations: we see that a very small percentage of absorbing carbon on otherwise nonabsorbing alumina enhances the particle emissivity and essentially determines its radiative properties. Also note that for single particles with sizes comparable to the wavelength, emissivities greater than one are possible.[11] This occurs because the particle can absorb radiation well beyond its geometrical confines. From Eq. (3), if the absorption cross section is larger than the geometrical cross section, emissivity greater than unity results.

Reversing the roles of the materials, i.e., calculating the emissivity for an alumina-coated carbon particle, we obtain the results shown in Fig. 4. It is seen that the emissivity of a particle having a carbon core of radius 1.96 μm and an alumina shell of thickness 0.04 μm is not drastically different from that of a pure carbon particle. We obtain the result that a thin shell of alumina on a carbon particle has far less effect on emissivity than does a thin shell of carbon on an alumina particle. As a matter of fact, even when the alumina shell is increased to a 1.0 μm thickness, the magnitude of the emissivity has only changed by approximately 10% from that of a pure, $r = 2$ μm carbon particle. Even more dramatic is the result obtained for a core containing less than 1% carbon and the rest, which corresponds to a thickness of 1.6 μm, alumina; the emissivity is still quite high and is approximately equal to that due to the same amount of carbon deposited on the surface of an alumina particle. Reduction of the carbon core to a radius of 0.05 μm, bottom spectrum in Fig. 4, yields approximately the same emissivity result as the pure alumina particle.

Rieger, in qualitative agreement with our experimental observations and theoretical calculations, has pointed out that the exhaust alumina from a rocket might contain small amounts of unburned aluminum and that this small fraction of absorbing material might be responsible for the anomalous emission from rocket plumes. To facilitate the computations, Rieger considered composite alumina-aluminum particles several times smaller than the wavelength, for which Rayleigh limit scattering is appropriate. (This means only the leading term given in Eqs. (1) and (2), namely, the electric dipole a_1, is retained.) Here we present the results for realistic particles[13] with size of the same order as the wavelength. Wavelength-dependent complex refractive indices are used for both materials—for alumina the same values used above, for aluminum refractive indices and extinction coefficients given in Ref. 14.

The results are, of course, similar to the carbon-alumina calculations, however, because of the larger value for the real part of the index of refraction of aluminum, the particles are better scatterers; therefore, the amount of absorbed energy is lower. Figure 5 shows the emissivity spectra for Al/Al_2O_3 particles with aluminum cores with radii of 1.5, 0.4, and 0.1 μm. We see again that a small quantity of absorbing material, 1% or less of aluminum, imbedded as a sphere in the middle of a weak absorber dominates the particle's emissive properties.

Conclusion

We have presented calculated infrared emissivity spectra for composite particles of alumina-carbon and alumina-aluminum. The calculations were motivated by the anomalous emissive properties experimentally observed for Al_2O_3 particles coated with a very thin layer of contaminant. Our results show that less than 1% by volume of absorbing carbon on the surface of a 2 μm radius alumina particle enhances that particle's emissivity by approximately three orders of magnitude. The same amount of carbon, if trapped inside to form the core of the composite particle, still essentially determines the infrared emissive properties of the particle. Similar results were also presented for alumina-aluminum composite particles.

In view of these experimental and theoretical results, it appears likely that the high radiance observed in rocket plumes containing aluminum particles is due to impurities, specifically unburned metallic aluminum and/or carbon.

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