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Normal-directional and normal-hemispherical reflectances of micron- and submicron-sized powder beds at 633 and 790 nm

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A conic pyroelectric detector is employed to measure the effective reflectances of powder beds of metals, SiC, WC, and graphite. The experimental results are compared with numerical solutions of the radiation transfer equation in a half-infinite homogeneous body with effective radiative properties. The effective albedo and phase function are theoretically estimated by the model of opaque particles with specularly or diffusely reflecting surfaces in the assumption of geometrical optics. The studied powder beds with particles of several tens of microns in diameter are generally described by the model where specular reflection by particle surfaces is assumed corresponding to refraction and extinction indices of materials in the dense form. The model does not apply to semitransparent particles of SiC. The powder beds of submicron particles of SiC and WC are highly agglomerated and consist of clusters of particles with diameters of several tens of microns. A submicron powder bed is found to be considerably less reflective than a micron-sized powder bed of the same material. This is described by the model where the agglomerates of submicron particles are treated as large particles with diffusely reflecting surfaces. The effective normal-hemispherical reflectance of a micron-sized powder bed correlates with the hemispherical reflectance of dense material. The observed differences between the experiment and the model can be explained by a systematic error at calibration, oxidation of materials, and diffraction effects. © 2006 American Institute of Physics. [DOI: [10.1063/1.2205358](https://doi.org/10.1063/1.2205358)]

I. INTRODUCTION

Laser heating of powder beds is a principal process in material technologies as selective laser sintering and melting^{1–3} and laser cladding.^{4,5} Light absorption and scattering in powder beds are important for heat transfer and related kinetics of binding. Powders applied for laser treatment were experimentally studied in Ref. 6. The reflectance of a loose powder bed can be significantly less than the reflectance of the corresponding dense material.⁶ Correlations between light extinction in powder beds and their structures were discussed in Ref. 7. Relative measurements of reflectance of powders were also reported using infrared spectroscopy.⁸ However, Ref. 8 did not focus on the relation between the optical properties of materials in powder and dense forms. The bidirectional reflectance and transmittance of water suspensions of fine polystyrene spheres were studied in Ref. 9.

Reflection of light by the surfaces of dispersed media such as powder beds is determined by radiation transfer inside them. Multiple scattering in dispersed systems is well studied only at low concentrations of scattering centres.¹⁰ At high concentration, so-called dependent effects were found,^{9,11} for example, interference of waves scattered by neighboring particles. In the limit of geometrical optics at a high ratio of particle diameter to radiation wavelength, dependent scattering can be explained by free transportation of radiation inside transparent particles¹² and its exclusion from opaque particles.⁷ Ray tracing Monte Carlo simulation^{13,14} and continuum two-flux modeling⁷ of radiation transfer in the near-surface absorption layer of a packed bed of opaque particles revealed a correlation between reflectances of powders and dense materials that agrees with experimental data.⁶

The objective of the present study is to extend the range of wavelengths and materials and to analyze the angular distributions of reflected radiation. This will provide more information about scattering mechanisms.

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FIG. 1. Experimental setup for measuring the normal-directional reflectance of the powder bed: d , base diameter of the conic detector; l , distance between the detector and the sample; and θ , maximum reflection angle of collected radiation.

II. EXPERIMENTAL PROCEDURE

The reflectance of powders was previously measured with an integrating sphere.⁶ This technique did not give the angular distribution of the reflected radiation. To obtain it, another experimental setup was used in this work (see Fig. 1). A collimated laser beam passed through a small hole at the vertex of a conic pyroelectric detector and struck the surface of a loose powder bed at normal incidence. The support of the powder sample was attached to a micrometer screw and could be displaced in the vertical direction. This changed the distance l between the powder surface and the detector base. The detector was made of a polyvinylidene fluoride (PVDF) pyroelectric film with a thickness of about $30\text{ }\mu\text{m}$. The inner surface of the cone was painted black to diminish the influence of the radiation reflected by the detector. The base diameter of the detector cone was $d = 28.5\text{ mm}$. The measurements were done with a lock-in amplifier. Two lasers with different wavelengths were used (see Table I). The pyroelectric cone integrates all the radiation reflected by the sample within a reflection angle θ , where

$$\tan \theta = \frac{d}{2l}. \quad (1)$$

TABLE I. Laser characteristics.

Manufacturer	Opto Power Corporation	Uniphase
Model	CJ-042, cw diode laser	1135P, He-Ne laser
Wavelength (nm)	790	633
Power (mW)	100	10

The reflected radiation can be characterized by its angular intensity¹⁵ $I(\theta) = F/S/\Omega$, where F is the energy flux through a surface element transferred by radiation directed within a small solid angle Ω around polar angle θ . Here, S is the area of the surface element projection to the direction of radiation propagation. The effective normal-hemispherical reflectance ρ_e is defined as the directional-hemispherical reflectance¹⁵ at normal incidence. It is equal to the ratio of total energy flux reflected in all directions to incident energy flux Q_i per unit surface,

$$\rho_e = \frac{2\pi}{Q_i} \int_0^1 I(\theta) \cos \theta d \cos \theta. \quad (2)$$

The normal-hemispherical reflectance of the sample is obtained at $l=0$ when the detector collects all reflected radiation.

The effective normal-directional reflectance $\rho_e'(\theta)$ corresponds to the directional-directional reflectance¹⁵ at normal incidence. It is defined as the ratio of angular intensity at a reflection angle θ to reference intensity that would be formed if the sample diffusely reflected all incident radiation. The reference intensity is independent of the angle θ and is found from energy conservation as Q_i/π . This gives the following relation:

$$\rho_e'(\theta) = \frac{\pi I(\theta)}{Q_i}. \quad (3)$$

The normal-directional reflectance of the sample is derived from the variation of the pyroelectric signal with the distance sample-detector l .

The pyroelectric signal was calibrated with highly reflective micron-sized alumina (Al_2O_3) powder (number 11 in Table II). Similar powder was studied in Ref. 6 where a value of 0.96 was obtained for the normal-hemispherical reflectance at a wavelength of $1.06\text{ }\mu\text{m}$. Since alumina is transparent in the range from 633 nm to $1.06\text{ }\mu\text{m}$ with no significant change in refraction index (see Ref. 16), one cannot expect a strong variation in the reflectance of this powder. The normal-hemispherical reflectance of micron-sized alumina powder was accepted to be 0.95 at 633 and 790 nm . A diffuse reflection law is assumed for this powder, so that the normal-directional reflectance is independent of the reflection angle and equal to 0.95.

III. RESULTS

The properties of the studied powders along with the measured normal-hemispherical reflectances at 633 and 790 nm are listed in Table II. Figure 2 shows micrographs of selected powders obtained by scanning electron microscopy (SEM). The spherical iron and copper powders are made by gas atomization at the MTM department of K.U. Leuven. The other powders are commercially available. The stainless steel powders 4 and 5 are of the type 316L. The composition of the aluminum alloy for powder 6 is 17.5 wt % Si, 5.5 wt % Fe, 3.1 wt % Cu, 1 wt % Mg, 0.56 wt % Zr, balance Al. Powders 8 and 9 were oxidized powders, while

TABLE II. Properties of studied powders and their effective normal-hemispherical reflectances ρ_e at 633 and 790 nm.

No.	Material	Particle size	Particle shape	Relative density	Reflectance at 633 nm	Reflectance at 790 nm
1	Fe	125–160 μm	spherical	0.55	0.228 $\pm$ 0.002	0.243 $\pm$ 0.002
2	Fe	30–58 μm	spherical	0.60	0.222 $\pm$ 0.002	0.253 $\pm$ 0.002
3	Fe	27–63 μm	irregular	0.33	0.161 $\pm$ 0.001	0.175 $\pm$ 0.002
4	Stainless steel ^a	37–61 μm	spherical	0.67	0.291 $\pm$ 0.001	0.313 $\pm$ 0.002
5	Stainless steel ^a	20–32 μm	spherical	0.54	0.246 $\pm$ 0.005	0.253 $\pm$ 0.005
6	Al alloy ^b	<200 μm	irregular	0.57	0.243 $\pm$ 0.002	0.233 $\pm$ 0.002
7	Cu, annealed	125–160 μm	spherical	0.58	0.641 $\pm$ 0.02	0.709 $\pm$ 0.002
8	Cu, oxidized	<50 μm	spherical	0.52	0.345 $\pm$ 0.02	...
9	Cu, oxidized	<25 μm	spherical	0.37	0.168 $\pm$ 0.01	...
10	Cu, annealed	<25 μm	spherical	0.37	0.521 $\pm$ 0.05	...
11	Al ₂ O ₃	<200 μm	irregular	0.30	0.95 ^c	0.95 ^c
12	Al ₂ O ₃	0.2 μm	irregular	...	0.964 $\pm$ 0.005	0.934 $\pm$ 0.002
13	SiC	<60 μm	irregular	0.50	0.135 $\pm$ 0.002	0.111 $\pm$ 0.001
14	SiC	<50 nm	agglomerated	...	0.058 $\pm$ 0.001	0.039 $\pm$ 0.001
15	WC	<45 μm	irregular	...	0.155 $\pm$ 0.005	0.158 $\pm$ 0.005
16	WC	0.2 μm	agglomerated	...	0.033 $\pm$ 0.001	0.038 $\pm$ 0.002
17	Graphite ^d	<15 μm	scalelike	...	...	0.054 $\pm$ 0.002

^aType 316L.^b17.5 wt % Si, 5.5 wt % Fe, 3.1 wt % Cu, 1 wt % Mg, 0.56 wt % Zr, balance Al.^cValues accepted for calibration.^dCarbon black.

powders 7 and 10 were annealed for 2 h in H₂ atmosphere at 300 °C to reduce the oxide layer. Powder 10 was prepared by annealing of powder 9.

The particle size of certain powders was estimated by laser diffraction using a Coulter LS100 apparatus. In these cases an interval such as “125–160 μm ” is shown in the third column of Table II with the first number d_{10} and the second number d_{90} where d_x means that the volume fraction of particles with diameter less than d_x is $x\%$. Otherwise the particle size is either estimated from a micrograph or supplied by a manufacturer. The particle shape is obtained from micrographs. For the submicron powders, these micrographs

show the presence of large agglomerates [see Figs. 2(h) and 2(i)]. The relative density specified in Table II is the ratio of the bulk density of loose powder to the theoretical density of the solid material. The bulk density is estimated from the weight of the powder that is inside the sample holder. Densities of solid metals are taken from Ref. 17. Theoretical densities of Al₂O₃ and SiC are accepted to be 4.0 and 3.21 g/cm³, respectively.

Figure 3 shows the measured normal-directional reflectance as a function of the reflection angle for the powders from Table II.

FIG. 2. SEM micrographs of powders: (a) irregular Fe 27–63 μm (No. 3); (b) spherical stainless steel 37–61 μm (No. 4); (c) spherical Cu <25 μm (No. 10); (d) irregular Al <200 μm (No. 6); (e) graphite (No. 17); (f) WC <45 μm (No. 15); (g) SiC <60 μm (No. 13); (h) SiC <50 nm (No. 14); and (i) WC 0.2 μm (No. 16).

IV. COMPARISON WITH THE THEORY OF RADIATION TRANSFER

The reflectance of a powder bed can be estimated theoretically by modeling radiation transfer in its near-surface layer.^{7,13} A common approach is to replace the powder bed by a homogeneous medium with effective absorbing and scattering properties in the half-space $z < 0$ and to solve the radiation transfer equation for angular radiation intensity $I(z, \theta)$,

$$\cos \theta \frac{\partial I}{\partial z} = \beta \left[\frac{\omega}{2} \int_{-1}^1 K(\theta', \theta) I(\theta') d \cos \theta' - I(\theta) \right], \quad (4)$$

where θ is the polar angle as shown in Fig. 1, z the coordinate along the external normal to the surface of the powder bed, β the extinction coefficient, and ω the albedo. The kernel^{7,15}

FIG. 3. Effective normal-directional reflectance ρ'_e of powder beds at the wavelengths of 790 (a) and 633 nm [(b)–(g)] as measured (points) and calculated (curves). Powder material and particle size and morphology are marked on the diagrams. Powder reference numbers are the same as in Table II. Solid-line curves are obtained assuming specular reflection at the surface of opaque particles with values of n and k specified in Table III. Broken-line curves correspond to the model of diffuse reflection with the given ρ and the scattering phase function P shown in diagram (h).

$$K(\theta', \theta) = \frac{1}{2\pi} \int_0^{2\pi} P(\alpha) d\varphi \quad (5)$$

is determined by the scattering phase function $P(\alpha)$ of the scattering angle α . This angle depends on the polar angles of incident radiation θ' and scattered radiation θ , and on the difference of azimuth angles φ as $\cos \alpha = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos \varphi$.¹⁵

Notice that the angular intensity of reflected radiation $I(\theta)$ used in Eqs. (2) and (3) is equal to $I(z, \theta)$ in Eq. (4) evaluated at $z=0$ and $\theta < \pi/2$. Therefore, Eq. (4) is numerically solved to estimate the effective reflectances ρ'_e theoretically. The results are plotted in Fig. 3.

One can introduce a dimensionless coordinate βz in Eq. (4) that excludes the parameter β . Only effective values of the albedo ω and the scattering phase function $P(\alpha)$ influence the angular distribution of radiation reflected by an optically thick powder bed. In the approximation of geometrical optics, the effective parameters of a dilute suspension of opaque spheres with specularly reflecting surfaces are estimated as¹⁵

$$\omega = \rho, \quad (6)$$

$$P = \rho' \left(\frac{\pi - \alpha}{2} \right) / \rho, \quad (7)$$

with $\rho'(\chi)$ the directional reflectance of the dense material. This value depends on the incidence angle $\chi = (\pi - \alpha)/2$. The hemispherical reflectance is

$$\rho = 2 \int_0^1 \rho'(\chi) \cos \chi d \cos \chi. \quad (8)$$

Monte Carlo simulation¹² suggests that Eqs. (6) and (7) also hold for closely packed beds of opaque spheres. A statistical scattering model⁷ gives the same result for packed beds of nonspherical particles. Therefore, we apply these equations to estimate the effective radiation transfer parameters of powder beds.

The directional reflectance of nonpolarized incident radiation is calculated from refraction n and extinction k indices by the Fresnel equations:¹⁵

$$\rho' = \frac{\rho_{\perp} + \rho_{\parallel}}{2}, \quad (9)$$

$$\rho_{\perp} = \frac{(nB - \cos \chi)^2 + (n^2 + k^2)A - n^2 B^2}{(nB + \cos \chi)^2 + (n^2 + k^2)A - n^2 B^2}, \quad (10)$$

$$\rho_{\parallel} = \frac{(n\Gamma - A/\cos \chi)^2 + (n^2 + k^2)A - n^2 \Gamma^2}{(n\Gamma + A/\cos \chi)^2 + (n^2 + k^2)A - n^2 \Gamma^2}, \quad (11)$$

$$A^2 = \left(1 + \frac{\sin^2 \chi}{n^2 + k^2} \right)^2 - \frac{4n^2 \sin^2 \chi}{(n^2 + k^2)^2}, \quad (12)$$

$$B^2 = \frac{n^2 + k^2}{2n^2} \left(\frac{n^2 - k^2}{n^2 + k^2} - \frac{\sin^2 \chi}{n^2 + k^2} + A \right), \quad (13)$$

TABLE III. Properties of dense materials at wavelengths of 633 and 790 nm: refraction n and extinction k indices and hemispherical reflectance ρ . Calculated effective normal-hemispherical reflectance ρ_e of powders at corresponding wavelengths.

Material	Wavelength (nm)	n	k	ρ	ρ_e
Al	633	1.4 ^a	7.6 ^a	0.90 ^b	0.417
	790	2.7 ^a	8.5 ^a	0.86 ^b	0.351
Cu	633	0.25 ^a	3.4 ^a	0.92 ^b	0.459
	790	0.25 ^a	5.0 ^a	0.96 ^b	0.568
Cu ₂ O	633	3.0 ^c	0.11 ^c	0.28 ^b	0.048
Fe	633	3.5 ^d	3.9 ^d	0.59 ^b	0.154
	790	3.7 ^d	3.9 ^d	0.59 ^b	0.152
Graphite	790	3.1 ^e	1.9 ^e	0.40 ^b	0.082
	790	2.0 ^f	0.7 ^f	0.21 ^b	0.029
SiC	633 and 790	2.6 ^a	0 ^a	0.23 ^b	0.037
WC	790	...	...	0.55 ^g	0.134

^aReference 16.

^bCalculated by Eq. (8).

^cReference 18.

^dReference 17.

^eOrdinary ray, Ref. 18.

^fExtraordinary ray, Ref. 18, at 619.9 nm.

^gReference 14, at 1.064 μm .

$$\Gamma = \frac{n^2 - k^2}{n^2 + k^2} B + \frac{2nk}{n^2 + k^2} \left(\frac{n^2 + k^2}{n^2} A - B^2 \right)^{1/2}. \quad (14)$$

The values of the indices for the relevant materials are taken from Refs. 16–18 and listed in Table III. The directional reflectances calculated by Eqs. (9)–(14) are plotted in Fig. 4 against the scattering angle $\alpha = \pi - 2\chi$, so that they are proportional to the scattering phase function P [see Eq. (7)]. Silicon carbide (SiC) is presented by a unique curve in Fig. 4 because its values of n and k are the same at 633 and 790 nm. The crystalline structure of graphite is highly anisotropic and its reflectance depends on the orientation of the electric field vector $\mathbf{E}$ relative to the crystallographic axes. Therefore, two different curves are given for graphite corre-

sponding to the ordinary ray with $\mathbf{E}$ in the basal plane and the extraordinary ray with $\mathbf{E}$ normal to the basal plane. There are no available data on n and k of tungsten carbide (WC). Directional reflectance of this material is supposed to be independent of the incidence angle. Hemispherical reflectances ρ obtained by numerical integration of Eq. (8) are also listed in Table III.

A. Normal-directional reflectance

Scattering phase functions specified by Eq. (7) have forward peaks at $\alpha=0$ and tend to plateaus in the backward hemisphere $\alpha > 90^\circ$, as shown in Fig. 4. For highly reflective metals as Al and Cu, the difference in directional reflectance between the peak and the plateau is small, so that scattering is approximately isotropic. The model of isotropic scattering would be appropriate for powder beds of such materials.^{7,15} Strongly forward-directed scattering is typical for opaque dielectric materials as SiC (see Fig. 4). However, numerical simulation of multiple scattering with such phase functions gives qualitatively similar angular distributions of radiation reflected by the surface of the powder bed both for metals and nonmetals: the effective normal-directional reflectance ρ_e' slightly increases with reflection angle θ (see full-line curves in Fig. 3). Sometimes a maximum is attained at θ slightly below 90° as for the upper curve in Fig. 3(a).

Similar angular distributions are experimentally obtained for micron-sized powders as shown, for example, in Figs. 3(a) and 3(b) (points). However, the value of reflectance given by the model is systematically less than the measured value. This may be due to drawbacks of both the experimental technique and the model. Experimental error can arise if the reflectance of alumina powder (powder 11 in Table II) used for calibration is overestimated. A questionable assumption of the model is the replacement of a powder bed by a homogeneous medium in Eq. (4) while the effective extinction length is known to be comparable with the particle size.⁷

FIG. 4. Directional reflectances ρ' of dense materials at 633 nm (broken lines) and 790 nm (full lines and a chain line) accepted for calculation of the effective normal-directional reflectances ρ_e of powders.

In the case of stainless steel [Fig. 3(b)], an additional error is possible because the values of n and k are taken for pure iron.

Experimental reflectance of annealed copper powders shown in Fig. 3(c) by dark symbols is, as for the other micron-sized powders, slightly higher than predicted by the model for pure Cu (upper curve). The reflectances of oxidized Cu powders (open symbols) are significantly lower and lie between model curves for copper (upper curve) and cuprous oxide (Cu_2O , lower curve). Powder 9 is finer than powder 8 and is likely to contain a higher fraction of Cu_2O . This explains its lower reflectance because the oxide is highly absorptive. The annealed powders may also contain a certain amount of Cu_2O that can be responsible for a small difference in reflectance between powders 7 and 10.

Figures 3(b) and 3(d) show that the difference between larger and smaller spherical particles is within the experimental error for iron and stainless steel micron-sized powders. The independence of the particle size corresponds to the model based on geometrical optics. The reflectance is considerably less in the case of irregular iron particles [powder 3 in Fig. 3(d)]. The particles of this powder are much larger than the radiation wavelength [see Fig. 2(a)]. However, light scattering on their sharp edges may deviate from geometrical optics and can cause a reduction in the effective reflectance relative to powders with spherical particles. An unexpectedly low reflectance is also observed for the irregular aluminium alloy (Al) powder in Fig. 3(e). The effect of irregular particle shape seems to be stronger in the case of Al because experimental points are even below the calculated curve. However, this discrepancy may also arise because the theoretical curve is calculated for pure aluminum and does not take into account the considerable amount of alloying elements.

A strong difference is observed between micron- and submicron-sized powders of the same material: beds of submicron powders are a lot more absorptive (compare powder 13 with powder 14 and powder 15 with powder 16 in Table II). Moreover, the angular distribution of reflected radiation is changed qualitatively in the case of submicron powders. The effective normal-directional reflectance decreases with reflection angle for powders 14 and 16 [Figs. 3(f) and 3(g)]. This change could be expected because of the completely different character of light scattering by particles with a size comparable with or less than the wavelength.¹⁰ Equations (6) and (7) cannot be employed in this case.

The SEM study of the submicron powders [see Figs. 2(h) and 2(i)] revealed two principal structural features of difference scales, which are the submicron particles themselves and their agglomerates of tens microns in size. The powder bed consists of packed agglomerates where an agglomerate consists of thousands of packed submicron particles.

Light scattering by these powder beds is analyzed at two scales too. At the scale of geometrical optics, scatterers are the agglomerates. The scattering model can be applied at this scale as in the case of the micron-sized powders. The difference is that the scattering on a micron-sized particle is determined by reflective properties of dense material but scatter-

ing on an agglomerate is the result of scattering on submicron particles it consists of. Thus, at the submicron scale, scattering by an agglomerate is determined by reflective properties of its surface constituting of submicron particles. Diffuse reflection by such an extremely rough surface seems to be a reasonable approximation. The scattering phase function is given by¹⁵

$$P = \frac{8}{3\pi}(\sin \alpha - \alpha \cos \alpha), \quad (15)$$

instead of Eq. (7). As shown in Fig. 3(h), diffuse reflection results in backward-peaked scattering. This is opposite to forward-peaked scattering at specular reflection (see Fig. 4) and can explain the decrease of the effective reflectance with increasing the reflection angle. Indeed, experimental results for SiC powder 14 and WC powder 16 are fitted by calculations with diffuse reflection [broken-line curves in Figs. 3(f) and 3(g)] at hemispherical reflectances ρ of the particle surface equal to 0.2 and 0.1, respectively.

One can consider micron-sized powders with irregular particles [see powders 3 and 6 in Figs. 3(d) and 3(e), respectively] as intermediate in reflectance between micron-sized powders with spherical particles and submicron-sized powders. A deviation from the result predicted by the model of specular reflection is clearly seen for the irregular iron powder where the reflectance shows a weak peak at reflection angles $\theta < 30^\circ$ [see Fig. 3(d)]. The angular distribution for irregular Al powder in Fig. 3(e) can be interpreted as having a peak or a plateau in the same range. A maximum at $\theta=0$ is typical for the model of diffuse reflection. Therefore, the results for irregular powders can be explained by a scattering phase function intermediate between those given by the models of specular (Fig. 4) and diffuse [Fig. 3(h)] reflections. This actually means a mixed specular/diffuse reflection at the surface of irregular particles.

Micron-sized SiC powder [13 in Fig. 3(f)] also has a reflection peak at small angles. Moreover, its reflectance is several times higher than predicted by the model of specular reflection (full-line curve). Such a large discrepancy cannot be attributed to a calibration error as in the case of metallic powders. The reason for this can be that SiC particles are, probably, not completely opaque, so that this model does not apply. After all, a ray striking a particle gives rise to a reflected ray and a refracted ray while this model takes only into account the reflected ray. This leads to an error in the case of a semitransparent particle since the refracted ray passes through the particle, exits from it at the backside, and also contributes to scattering. This increases the albedo ω of the powder and results in a raise of the effective reflectance.

B. Normal-hemispherical reflectance

Ray tracing Monte Carlo simulation¹³ and the two-flux model of multiple scattering⁷ indicate that the effective reflectance of a packed bed of opaque particles is a function of the reflectance ρ of the dense material. The two-flux model⁷ gives the effective normal-hemispherical reflectance as

FIG. 5. Effective normal-hemispherical reflectance of a powder bed ρ_e vs hemispherical reflectance of dense material ρ : experimental data (circles), numerical calculation with scattering phase functions corresponding to specular (crosses) and diffuse (points) reflection, and the analytical two-flux model for isotropic scattering (full line) and diffuse reflection (broken line). The vertical dotted lines mark values of ρ accepted for the given material and wavelength. Experimental and numerical points for graphite are referred to two different ρ corresponding to reflection of ordinary and extraordinary rays. Powder material, its number in Table II, wavelength, and other relevant information if necessary are shown near either experimental points or vertical dotted lines.

$$\rho_e = \frac{1 - \sqrt{1 - \rho}}{1 + 2\sqrt{1 - \rho}}, \quad (16)$$

for isotropic scattering with phase function $P=1$ corresponding to specular reflection with constant directional reflectance ρ' as shown for WC in Fig. 4, and

$$\rho_e = \frac{1}{4} \frac{1 + 3\rho - \sqrt{1 - \frac{2}{3}\rho - \frac{1}{3}\rho^2}}{1 + 2\sqrt{1 - \frac{2}{3}\rho - \frac{1}{3}\rho^2}}, \quad (17)$$

for diffuse reflection with the phase function given by Eq. (15) and shown in Fig. 3(h). These analytical functions are plotted in Fig. 5. In the case of specular reflection with the directional reflectance ρ' dependent on the angle of incidence, analytical result (16) is not rigorous and one can solve the radiation transfer equation (4) numerically to obtain ρ_e .

The numerical solution of Eq. (4) for the model of specular reflection (with directional reflectances shown in Fig. 4) gives effective normal-directional reflectances ρ_e listed in Table III and shown by crosses in Fig. 5. These crosses essentially lie on the full line corresponding to the model for isotropic scattering, Eq. (16), for reflectances $\rho > 0.8$. The phase function becomes more and more forward directed with decreasing ρ (see Fig. 4) and the numerical crosses deviate from the model of isotropic scattering. However, the difference remains surprisingly low even for SiC and graphite, which have a highly anisotropic scattering behavior. Numerical calculations for diffuse-reflection phase function, Eq. (15) (points in Fig. 5), are very close to the broken line obtained by the two-flux method, Eq. (17), for

the same phase function. The small deviation can be attributed to additional assumptions accepted in the two-flux model for multiple scattering.

Experimental data (circles in Fig. 5) are plotted versus reflectances of dense materials listed in Table III. Exceptions are submicron powders 14 and 16 with values $\rho=0.2$ and 0.1 , respectively, which fit to the experimental angular distributions of reflected radiation as found in Sec. IV A. Graphite is shown by two circles with the same ρ_e but different ρ corresponding to reflection of ordinary and extraordinary rays. The two limits can be hardly attained. Figure 2(e) shows that graphite flakes are randomly oriented in the powder bed, so that the average value of ρ should be somewhere between these points on the line connecting the points (see Fig. 5).

Experimental points for Al alloy (powder 6) are plotted in Fig. 5 against the reflectance of pure Al because the reflectance of this alloy in the dense state is unavailable in literature. It can actually be considerably less.¹⁹ One can estimate the reflectance by the theory of free electrons where the absorptance is proportional to the square root of the electrical resistance.¹⁹ Electrical resistance of Al alloy 390.0 with a similar composition as for the alloy studied in this work is about 2.5 times greater than the electrical resistance of pure Al.²⁰ This gives an estimation of the uncertainty in the reflectance of dense Al alloy shown by horizontal bars in Fig. 5.

The experimental data for micron-sized powders generally follow the curve calculated for isotropic scattering (full line in Fig. 5). The exception is SiC (powder 13) whose particles are expected to be partially transparent. Effective reflectances of metallic powders with spherical particles (powders 1 and 7) are slightly above the theoretical curve. In

the case of irregular particles (powders 3 and 6), the effective reflectance is somewhat less. Probable reasons for this were discussed in Sec. IV A. Submicron powders (14 and 16) are better described by the model of diffuse reflection (broken line in Fig. 5).

Similar correlations between the effective reflectance of powder bed and the reflectance of dense materials at wavelengths of 1.06 and 10.6 μm were discussed in Ref. 7.

V. DISCUSSION

The experimental results cannot be completely explained by the applied theory. Possible reasons for this are analyzed below.

A. Diffraction effects

Application of the radiation transfer equation (4) allows taking into account diffraction. The issue is estimation of the effective radiative properties of the medium, extinction coefficient β , albedo ω , and scattering phase function $P(\alpha)$. At multiple scattering by dilute suspension of spheres, these parameters are actually determined by scattering on a single sphere. Diffraction is rigorously calculated by the Mie theory.¹⁰ However, diffraction can be neglected when particles are much greater than the wavelength.¹⁵ This is the case for particles of several tens of microns. The contribution of diffraction in this case was quantitatively estimated in Ref. 21 where it was also shown that diffraction effects are negligible.

Concerning powder beds studied in the present work, principal questions arise about diffraction on sharp edges and corners of particles of irregular shape and so-called dependent scattering.^{7,12} The second effect is well known for packed beds where particles touch each other. This is, actually, a mutual influence of neighboring scatterers. A thin gap is formed near the point contact between two particles. The gap is comparable with the wavelength even if the particles are much larger than the wavelength. Thus, structure features appear where strong diffraction is possible. Rigorous models taking into account diffraction on edges, corners, and point contacts are not known. Therefore, the experimental data are compared with the dependent scattering model^{7,12} based on geometrical optics and resulting Eqs. (6) and (7). This model assumes that the radius of curvature of the boundary between the transparent and the opaque phases is much greater than the wavelength.⁷

Comparison of the experimental data with the model reveals qualitative contribution of diffraction. According to the model,⁷ albedo ω and scattering phase function $P(\alpha)$ are independent of particles' shape and size. Therefore, the normal-directional and normal-hemispherical reflectances should be independent too. Indeed, the beds of 125–160 μm (powder 1) and 30–58 μm (powder 2) iron spheres give practically the same normal-hemispherical reflectance, as shown in Fig. 3(d). In these cases, the only structure features comparable with the wavelength are contacts between particles. Therefore, one can conclude that diffraction on the contacts is negligible for the studied micron-sized powders.

On the contrary, a significant difference in the normal-directional reflectance is observed when spherical particles [powders 1 and 2 in Fig. 3(d)] are changed to the particles of irregular shape (powder 3). This can be attributed to diffraction on sharp edges and corners of irregular particles [see Fig. 2(a)].

A strong difference in normal-directional reflectance observed between micron-sized and submicron powders would clearly indicate diffraction on submicron particles. However, one should take into account a qualitatively different packing structure of submicron powders consisting of large agglomerates of particles [see Figs. 2(h) and 2(i)]. The adopted model of diffuse reflection by the surface of the agglomerates implicitly includes diffraction because reflection of light by a surface with a submicron-scaled roughness implies diffraction.

B. Estimation of refraction and extinction indices

The accepted values of the indices for the relevant materials are taken from Refs. 16–18 and listed in Table III. The indices of pure iron and copper are quite certain. There are several sources where the same or similar values are reported. In addition, these values correctly correlate with the data on reflectance of dense materials. Therefore, the uncertainty in the indices cannot be responsible for the deviation between the experiment and the theory for powders 1–3 and 7. However, oxidation of copper powders 8–10 is revealed to change their optical properties. The indices of the stainless steel and the Al alloy are not available in literature, so that the corresponding values for pure Fe and Al, respectively, were used for the model. The uncertainty of such an approach is estimated in Sec. IV B and shown in Fig. 5 for Al alloy. It can be responsible for the major part of the deviation between experimental and theoretical data for powders 4–6.

Only one reference has been found for the indices of SiC. However, the principal difficulty with this material is not the possible uncertainty in the indices but the fact that its particles are likely to be semitransparent while the model applies to completely opaque particles. No data on the indices have been found for WC. Therefore, the simplified model of isotropic scattering is applied for this material, which correctly explains the experimental data.

C. Experimental errors

The pyroelectric signal was calibrated with highly reflective micron-sized alumina powder, which reflectance was measured with the uncertainty of few percents in Ref. 6. This is too small to explain the deviation between our experiment and model. Alumina is transparent at the studied wavelengths. The reflectance of its powder should be sensitive to a small volumetric absorption due to admixtures and defects. The powders used in Ref. 6 and our experiment were likely taken from different manufacturers, so that they may contain different admixtures and kinds of defects. This is why the actual uncertainty can be much greater.

Spherical iron and annealed copper powders (1, 2, and 7) are the most appropriate for comparison with the model because they contain few structural features where strong dif-

fraction is possible and indices n and k are known with sufficient accuracy for these materials. The model was also validated for packed beds of opaque spheres by ray tracing simulation.⁷ The normal-directional reflectances of these powders shown in Figs. 3(a), 3(c), and 3(d) are superior to the model predictions (solid lines) by factors ranging from 1.3 to 1.6. If the reflectance of the alumina powder were about 0.6–0.7, the model would perfectly match the experiment.

The thicknesses of the powder beds are about 5 mm. This is sufficient to exclude the influence of the substrate. It was experimentally shown that radiation penetrates into powder beds of opaque particles up to the depth of several particle sizes only.²¹ In the case of transparent particles of alumina the penetration may be deeper. However, variation of the thickness of this powder around 5 mm did not result in variation of the signal.

The diameter of the laser beam was about 1 mm that ensures averaging over a great number of reflections by individual particles covered by the beam. The powder bed could be shifted parallel to its surface. Measurements of each powder were repeated several times with different parts of the powder bed surface irradiated by laser. The difference between these measurements was not important. This proves homogeneity of the studied powder beds at the scale of the laser beam diameter.

VI. CONCLUSIONS

Normal-directional and normal-hemispherical effective reflectances of powder beds are measured by a conic pyroelectric detector at wavelengths of 633 and 790 nm.

The experimental results are compared with numerical solutions of the radiation transfer equation in a half-infinite homogeneous body with effective radiative properties. The effective albedo and phase function are theoretically estimated by the model of opaque particles with specularly or diffusely reflecting surfaces in the assumption of geometrical optics.

The studied powder beds with particles of several tens of microns in diameter are generally described by the model where specular reflection by particle surfaces is assumed corresponding to refraction and extinction indices of materials in the dense form. The only exception found is the micron-sized SiC powder, which reflects several times more than predicted by the model. The particles of SiC may be partially transparent and under these conditions the model does not apply.

The studied powder beds of submicron particles of SiC and WC are highly agglomerated and consist of clusters of particles with diameters of several tens of microns. A submicron-sized powder bed is found to be considerably less reflective than a micron-sized powder bed of the same material. This is described by the model where the agglomerates of submicron particles are treated as large particles with diffusely reflecting surfaces.

The effective reflectance of a powder bed of micron-sized Fe particles of irregular shape is slightly less than in

the case of spherical particles. The angular distribution of the radiation reflected by the irregular powder has features typical for the model of diffuse reflection. The effective reflective properties of this powder are intermediate between micron-sized and submicron-sized powders and qualitatively correspond to a mixed specular/diffuse reflection by particle surfaces.

The effective normal-hemispherical reflectance of a micron-sized powder bed correlates with the hemispherical reflectance of the corresponding material in the dense form. A similar relation is expected for the agglomerated powder beds of submicron particles.

The observed differences between the experiment and the model can be explained by a systematic error at calibration. Oxidation of several metallic powders is responsible for these deviations too. The apparent discrepancies for the stainless steel and Al alloy powders are possibly related to inaccurately estimated optical properties of these alloys, which are not available in literature. Diffraction on sharp corners and edges contributes to the discrepancy between the model and the experiment for irregular particles. Also, diffraction effects are implicitly taken into account by the diffuse scattering model for the agglomerated submicron powders.

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