JTTEE5 9:478-482

Peer Reviewed

Anisotropic Thermal Conductivities of Plasma-Sprayed Thermal Barrier Coatings in Relation to the Microstructure

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(Submitted 25 February 2000)

Anisotropic thermal conductivities of the plasma-sprayed ceramic coating are explicitly expressed in terms of the microstructural parameters. The dominant features of the porous space are identified as strongly oblate (cracklike) pores that tend to be either parallel or normal to the substrate. The scatter in pore orientations is shown to have a pronounced effect on the effective conductivities. The established quantitative microstructure-property relations, if combined with the knowledge of the processing parameters-resulting microstructure connections, can be utilized for controlling the conductivities in the desired way.

Keywords anisotropy, microstructure, thermal barrier coating, thermal conductivity, thermal spray

1. Introduction

The present work aims at relating the anisotropic thermal conductivities of plasma-sprayed coatings to their microstructure. These relations are derived in the explicit quantitative form, in terms of the appropriate microstructural parameters. Such parameters reflect shapes and orientational distributions of pores (including the orientational scatter, which is shown to play an important role).

Our approach allows one to model pores as inclusions that have nonzero thermal conductivities (different from the one of the virgin material). The present work, however, models the pores as insulators. This simplification can be viewed as the first approximation that can be refined, if needed. Another simplification assumed in the present work is that the effect of pores on the radiative heat transfer is not considered (since, however, the pores typically have flat, cracklike shapes, this effect can be expected to be secondary, as compared to the influence of pores on the conductivity).

We establish a quantitative connection between the structure of the porous space and the effective conductivities. A utility of our work can be viewed as follows: a progress in the understanding of the relationship between the processing parameters and the resulting microstructure (not a subject of the present work) can be translated into controlling the anisotropic conductivities in the desired way.

Note that, although the present work discusses the thermal conductivities, the results can be reformulated for the problem of the dielectric permeabilities as well. We also add that the microstructure, *mechanical* properties relations similar to the ones established here for the *thermal* properties, is given in a companion paper[1]

For the porous solids, in general, the literature on conductivity is quite substantial. We mention only the pioneering work of Bristow[2] on the conductivity of microcracked materials and the works of Thorpe[3] and Shafiro and Kachanov[4] on the conductivity of materials with pores of various shapes.

As far as sprayed coatings are concerned, the effective conductivities have been investigated in a number of works. McPherson[5] estimated the loss of conductivity in the direction normal to the substrate in terms of loss of the contact area between layers (contact zones being isolated circular “islands”). The drawback of the modeling based on contact area reduction is that it does not account for the orientational scatter of the pores—an important factor, as shown in the present work. (Besides, it does not address the effective conductivity loss in the direction parallel to the substrate). In the review of Doltsinis *et al.*,[6] finite element modeling of the effective conductivity of coatings was discussed. Note that the effective diffusivity of coatings—the problem that is mathematically similar to the one of conductivity—was discussed by Boire-Lavigne *et al.*,[7] who adapted the contact area approach of McPherson, and, from the experimental point of view, by Cernuschi *et al.*[8]

2. Modeling of the Coating Microstructure

Plasma-sprayed ceramic coatings have a lamellar microstructure consisting of elongated, flatlike splats of diameters of the order of 100 to 200 m and thicknesses of 2 to 10 m, formed by a rapid solidification. The porous space comprises micropores and microcracks of diverse shapes and orientation. Overall, it has a highly anisotropic structure that results in anisotropic reduction of thermal conductivity, as compared to the one of the bulk material.

For modeling of the effective thermal conductivities, the complexity of the porous space has to be reduced to several dominant elements. Following Bengtsson and Johannesson,[9] Leigh and Berndt,[10] Sevostianov and Kachanov,[2] as well as a number of earlier works, we identify the dominant elements of the

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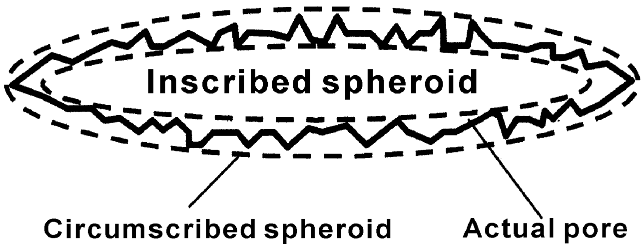

Fig. 1 Bounding the jagged pore shapes by the inscribed and circumscribed spheroids

porous space as two families of strongly oblate spheroidal pores, approximately parallel and approximately perpendicular to the substrate.

The actual microstructures of plasma-sprayed coatings are quite irregular. The following kinds of irregularities can be identified.

(A) Pores have "jagged" contours and resemble spheroids only approximately. This factor is, however, of minor importance for the effective properties and does not preclude modeling of pores by spheroids. Indeed, the results of Huet *et al.*[11] show that the replacement of pores (or, more generally, inclusions) by the shapes that are inscribed and circumscribed (Fig. 1) generates lower and upper bounds for the effective thermal conductivities. Since, as shown below, the contribution of a strongly oblate pore to the overall conductivities is almost independent of its aspect ratio γ (up to $\gamma = 0.15$), bounding of the jagged pores by the inscribed and the circumscribed ones (both remaining strongly oblate) generates bounds that are very tight and thus justifies modeling of pores by oblate spheroidal pores.

(B) Besides having jagged contours, cracklike pores may be substantially noncircular in plane. Nevertheless, they can be replaced by equivalent penny-shaped cracks provided the deviations from the circular shape are random.[12]

(C) Although the pores *tend* to be parallel or perpendicular to the substrate, their actual orientations have a substantial scatter. This orientational scatter may have a pronounced effect on the overall thermal and elastic properties. Thus, in contrast with the irregularity factors (A) and (B), the orientational scatter has to be accounted for. We model it by an appropriate orientation distribution function, as follows.

Modeling pores by (strongly oblate) spheroids, we express the unit vector n along the spheroid's symmetry axis in terms of two angles $0 \le \varphi \le \pi/2$ and $0 \le \theta \le 2\pi$ with respect to a fixed coordinate system: $\boldsymbol{n}(\varphi, \theta) = \cos\theta \sin\varphi \boldsymbol{e}_1 + \sin\theta \sin\varphi \boldsymbol{e}_2 + \cos\varphi \boldsymbol{e}_3$ and characterize the orientational distribution of pores by the probability density function $P(\varphi, \theta)$. Following Shafiro and Kachanov,[4] we introduce an orientational distribution that is *intermediate* between the random and the parallel ones; *i.e.*, it has a certain orientational preference but possesses a scatter that is characterized by the parameter λ:

$$P_\lambda(\varphi) = \frac{1}{2\pi}\left[\left(\lambda^2 + 1\right)e^{-\lambda\varphi} + \lambda e^{-\lambda\pi/2}\right] \qquad \text{(Eq 1)}$$

(the independence of θ implies the transverse isotropy, with the plane parallel to the substrate being the isotropy plane). Parameter $\lambda \ge 0$, which characterizes the sharpness of the peak at $\varphi = \pi/2$, quantifies the extent of the scatter. The limiting cases of the fully random and ideally parallel pores correspond to $\lambda = 0$ and $\lambda = \infty$, respectively. Figure 2 shows the orientational patterns that correspond to several values of λ.

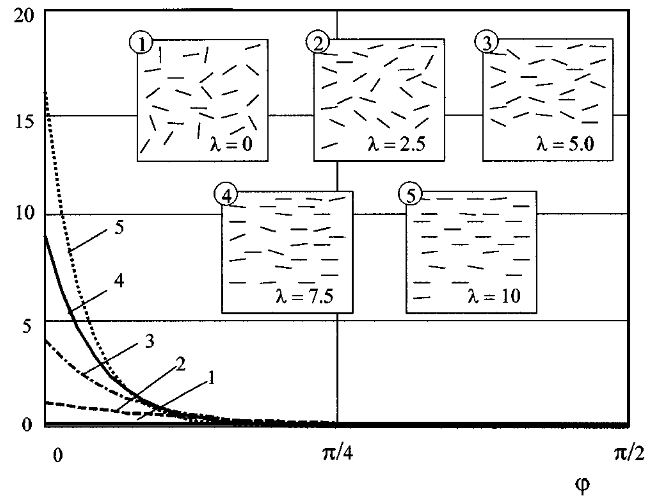

Fig. 2 Dependence of the orientational distribution function P_λ on angle φ at several values of λ and the corresponding orientational patterns

As discussed by Kachanov *et al.*,[13] the material properties are relatively insensitive to the exact form of the function that has the above-mentioned features. Eq. 1 is chosen to keep the calculations, related to averaging over orientations, simple.

3. Theoretical Background

We consider a material with a large number of pores. Assuming that the virgin material is thermally isotropic (with conductivity k_0), we seek to express the effect of pores on the overall conductivity in terms of appropriate parameters that characterize the shapes, the concentration, and the orientational distribution of pores. If the pores are nonspherical and have certain preferential orientation—the situation typical for the plasma-sprayed coatings—then the overall conductivity is anisotropic. Therefore, it has to be expressed in terms of the conductivity tensor, K_{ij} which relates the overall heat flux vector Q_i to the temperature gradient G_j vector (in the anisotropic case, these two vectors are, generally, not collinear):

$$Q_i = K_{ij}G_j \qquad \text{(Eq 2)}$$

The problem to be addressed is to express the effective conductivities in terms of the appropriate microstructural parameters.

We now briefly outline the relevant background results, keeping mathematics to the bare minimum and referring the reader to the work of Shafiro and Kachanov[4] for details. We first consider a reference volume V of a material containing one cavity. In the present work, the cavity is modeled as an ideal insulator (although the analysis can be extended, in a straightforward way, to pores filled with a conducting gas). The change of heat flux vector ΔQ_i (per volume V) due to the cavity is a linear function of the far-field temperature gradient G_j and hence can be written in the form

$$\Delta Q_i = H_{ij} G_j \qquad \text{(Eq 3)}$$

where the tensor H_{ij} depends on the pore shape. For the *oblate spheroidal cavity,* the shape relevant for plasma-sprayed coatings,

$$H_{ij} = -\frac{V_{\text{cav}}}{V}\, k_0 (A_1 \delta_{ij} + A_2 n_i n_j) \qquad \text{(Eq 4)}$$

where the shape factors A_1 and A_2—functions of the pore aspect ratio γ—are plotted in Fig. 3.

In the limit of a circular *crack* ($\gamma \rightarrow 0$),

$$H_{ij} = -\frac{8a^3}{3V}\, k_0 n_i n_j \qquad \text{(Eq 5)}$$

An important observation is that the strongly oblate pores (aspect ratios up to $\gamma = 0.15$) can be replaced, with good accuracy, by cracks, as far as their impact on the overall conductivities is concerned (a similar result holds for the impact of pores on the *elastic* properties). Indeed, Fig. 3 shows that, of the two shape factors, $V_{\text{cav}}A_1$ and $V_{\text{cav}}A_2$ entering Eq 5, the first one is negligibly small and the second one remains almost constant, as long as the aspect ratio $\gamma < 0.15$.

For a material with many pores, the simplest calculation of the overall conductivity is given by the so-called approximation of noninteracting pores. In this approximation, each pore is subject to the same far-field temperature gradient, unperturbed by the presence of neighbors. Then, the contributions of individual pores to the change of the overall conductivity $K_{ij} - k_0\,\delta_{ij}$ are simply added up, so that the effective conductivities

$$K_{ij} = k_0 \delta_{ij} + \sum_m H_{ij}^{(m)} \qquad \text{(Eq 6)}$$

In the important case of *cracks* (aspect ratio $\gamma = 0$),

$$K_{ij} = k_0(\delta_{ij} + 8\alpha_{ij}/3) \qquad \text{(Eq 7)}$$

where α_{ij} is the *crack density tensor,*[14] which characterizes the density of cracks taking into account their orientational distribution ($a^{(m)}$ is mth crack radius).

$$a_{ij} = 1/V \sum \left(a^3 n_i n_j\right)^{(m)} \qquad \text{(Eq 8)}$$

Note that its trace

$$\rho = \alpha_{u} = 1/V \sum a^{(m)3} \qquad \text{(Eq 9)}$$

is the usual scalar crack density parameter, which is adequate in the case of random crack orientations (overall isotropy).

The noninteraction approximation remains adequate at low concentration of pores, when the interactions between pores can be neglected. To account for the impact of interactions between

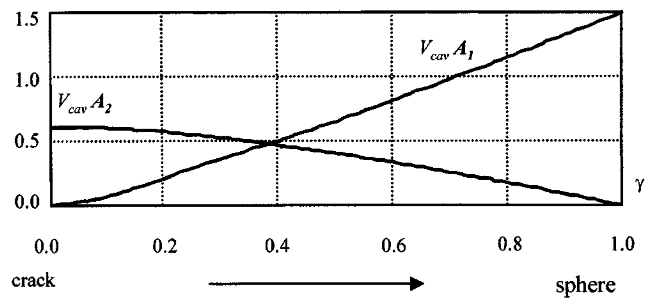

Fig. 3 Shape factors (entering expression 2) as functions of the pore aspect ratio

the individual pores on the overall conductivity, we utilize a relatively simple Mori-Tanaka's scheme, which is adequate, provided the mutual positions of pores are more or less random (for example, pores do not form periodic arrangements). This scheme takes the interactions into account by subjecting each pore to the temperature gradient that is increased by porosity by a factor of $(1 - p)^{-1}$, as compared to the far-field one, where p is porosity (the volume fraction of pores). Then, instead of Eq 6, we have

$$K_{ij} = k_0\, \delta_{ij} + \frac{1}{1-p} \sum_m H_{ij}^{(m)} \qquad \text{(Eq 10)}$$

The correction for interactions $(1 - p)^{-1}$ is relatively mild (as long as the overall porosity does not exceed 15 to 20%) and vanishes in the limit of cracks ($p \rightarrow 0$).

Physically, this is explained by the fact that the interactions between the individual pores may produce opposite effects: *shielding* (the combined contribution of a pair of interacting pores into the overall conductivity is *lower* than a sum for the two *noninteracting* pores), which is typical for the "stacked" arrangements; and *amplification,* which is typical for the arrangements of collinear type. In the case of *cracks,* these two opposite modes of interactions balance each other, so that the overall conductivity remains the same as in the noninteraction approximation. In the case of pores of nonzero porosity p, the overall balance is tilted toward the amplification mode, as reflected by the multiplier $(1 - p)^{-1}$ in Eq 10.

Thus, in the case of strongly oblate pores (relevant for the plasma-sprayed materials), their impact on the overall conductivity is mainly characterized by replacing the pores by cracks, with the correction $(1 - p)^{-1}$ for interactions, and the effective conductivities are given by

$$K_{ij} = k_0 \delta_{ij} - 8 k_0 a_{ij}/3(1 - p) \qquad \text{(Eq 11)}$$

reflecting that the effect of the crack term α_{ij} is enhanced by porosity.

4. Results

We now calculate the anisotropic effective conductivities of a coating. We denote by x_3 the axis normal to the substrate, so

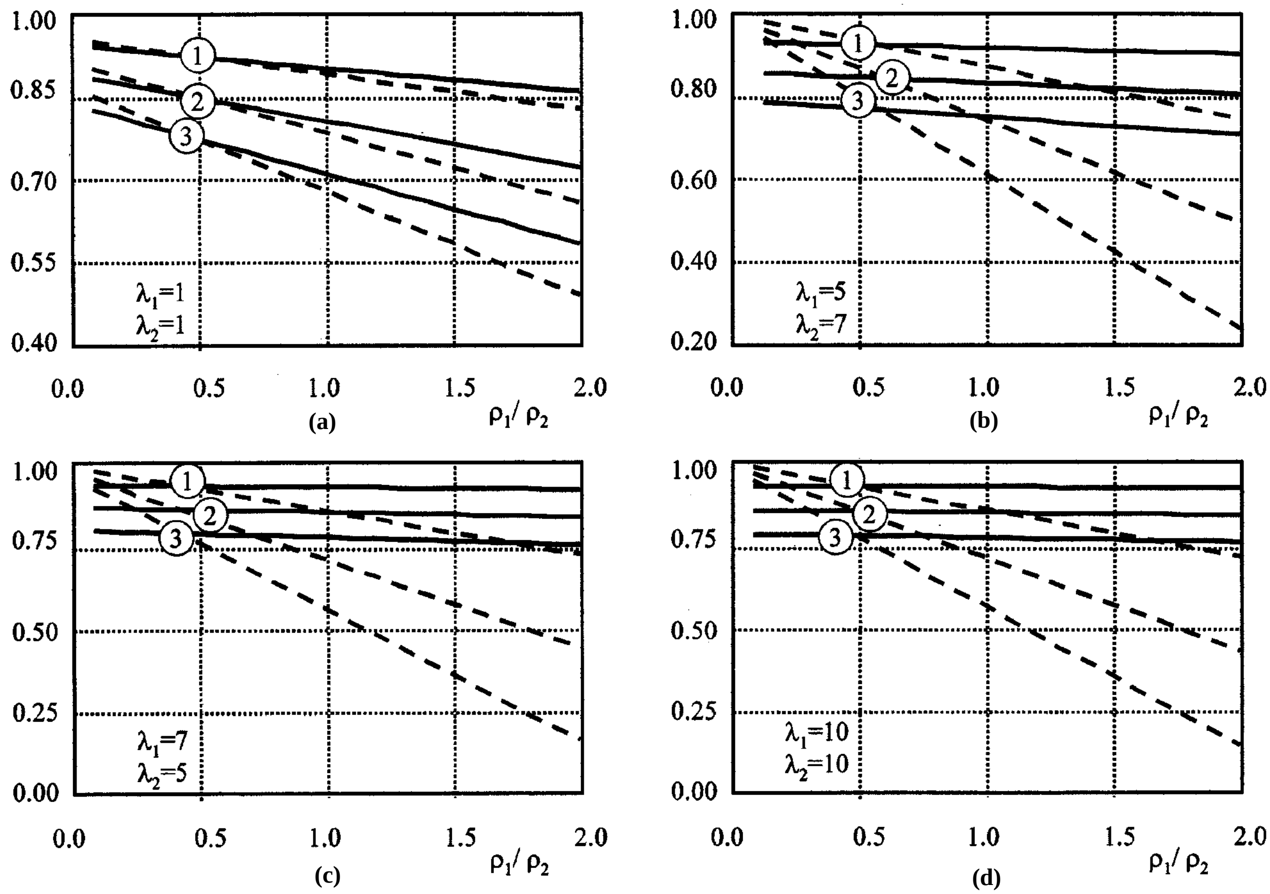

Fig. 4 (a) to **(d)** The effective conductivities $k_{11} = k_{22}$ (solid lines) and k_{33} (dashed lines) as functions of partial crack densities ρ_1 and ρ_2 of the horizontal and vertical crack systems for several values of scatter parameters λ_1 and λ_2. Symbols 1, 2, and 3 stand for ρ_2 = 0.05, 0.1, and 0.15.

that x_1x_2 is the plane of isotropy. The overall conductivity of the coating is transversely isotropic: $K_{11} = K_{22} \neq K_{33}$. We seek to express K_{11} and K_{33} in terms of the microstructural parameters.

As discussed above, the porous space is modeled by two families of penny-shaped cracks—"horizontal" and "vertical"—that tend to be parallel or perpendicular to the substrate. Both families can be characterized by the orientational distribution function (Eq. 1) (the distribution functions for these two families differ by shifting angle φ on $\pi/2$) with generally different scatter parameters λ_1 and λ_2. Averaging over orientations yields the following expressions for the components of the crack density tensor:

$$a_{11} = a_{22} = \frac{1}{2}(f_2(\lambda_2) + f_1(\lambda_2))\rho_2 + f_1(\lambda_1)\rho_1$$
$$a_{33} = f_1(\lambda_2)\rho_2 + f_2(\lambda_1)\rho_1 \qquad \text{(Eq 12)}$$

where $\rho_{1,2}$ are partial crack densities for the two families:

$$\rho_1 = \frac{1}{V}\sum a_{(1)}^{3\ (m)}; \rho_2 = \frac{1}{V}\sum a_{(2)}^{3\ (m)} \qquad \text{(Eq 13)}$$

and $f_{1,2}$ are functions of the scatter parameters:

$$f_1(\lambda) = \frac{18 - \lambda(\lambda^2 + 3)e^{-\lambda\pi/2}}{6(\lambda^2 + 9)};$$
$$f_2(\lambda) = \frac{(\lambda^2 + 3)(3 + \lambda e^{-\lambda\pi/2})}{3(\lambda^2 + 9)} \qquad \text{(Eq 14)}$$

Then, according to Eq 11, the effective conductivities are

$$K_{11} = K_{22} = k_0\left(1 - \frac{8}{3}\frac{\alpha_{11}}{1-p}\right); \quad K_{33} = k_0\left(1 - \frac{8}{3}\frac{\alpha_{33}}{1-p}\right) \qquad \text{(Eq 15)}$$

with α_{11} and α_{33} given by Eq 13.

Importantly, the characteristics of the porous space that determine the overall conductivity are reduced to only two parameters—components α_{11} and α_{33} of the crack density tensor (with porosity p playing a secondary role *via* the correction multiplier $(1 - p)^{-1}$). These two parameters reflect *both* the partial crack densities ρ_1 and ρ_2 of the two pore families *and* their orientational scatters λ_1 and λ_2. Physically, this is explained by the fact that the orientational scatter of the horizontal pores produces the same effect as the reduction of density of the horizontal pores plus the increase of density of the vertical pores (formulas in Eq 12).

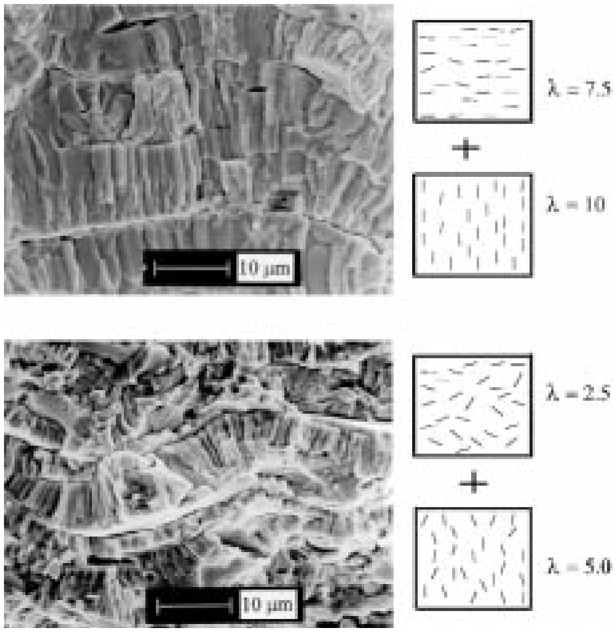

Fig. 5 Two coating microstructures corresponding to temperatures 800 and 400 °C of the substrate and their modeling by two families of strongly oblate pores. Scatter parameters $_1$ and $_2$ are chosen to match the observed patterns. (Photographs are taken from Ref 2, with permission of ASM International, Materials Park, OH)

The dependence of effective conductivities $K_{11} = K_{22}$ and K_{33} on partial crack densities ρ_1 and ρ_2 for several values of the scatter parameters λ_1 and λ_2 is illustrated in Fig. 4.

5. Discussion and Conclusions

The highly anisotropic structure of the porous space of the plasma-sprayed coatings (strongly oblate pores that tend to be either parallel or normal to the substrate) results in the anisotropy of thermal conductivity. Our results explicitly express the anisotropic conductivities $K_{11} = K_{22}$ and K_{33} in terms of the proper microstructural parameters and identify these parameters as components α_{11} and α_{33} of the crack density tensor that incorporate both the partial crack densities ρ_1 and ρ_2 of the two pore families and their orientational scatters.

Thus, our analysis implies that the quantitative characterization of the porous space can be reduced to only two parameters, α_{11} and α_{33}. It further implies that neither the partial porosities of the two pore systems nor the overall porosity p constitutes the proper parameters in terms of which the effective conductivities can be expressed. Physically, it is clear that, if the aspect ratios of narrow, strongly oblate pores are changed, say, from 0.05 to 0.10, such a change would double the porosity, but would produce only a negligible impact on the effect of pores on the overall conductivities.

The proper microstructural parameters α_{11} and α_{33} disregard the aspect ratios of the pores and treat them as cracks. The overall porosity p plays only a secondary role (through a multiplier $(1 - p)^{-1}$, as compared to the dominant contribution of the crack parameters α_{11} and α_{33}.

Our analysis demonstrates a substantial influence of the orientational scatter of pores (parameters λ_1 and λ_2) on the overall conductivities, since they noticeably affect the values of α_{11} and α_{33}. Therefore, a sufficiently accurate determination of the orientational scatter of pores can be identified as an important challenge that has to be addressed. It appears that, presently, such a determination (from microphotographs) can be done only approximately (Fig. 5).

The obtained results directly relate, in quantitative terms, the thermal barrier coating performance of plasma-sprayed coatings to the microstructural parameters. Therefore, they provide the theoretical framework for optimization of the technological parameters that control microstructure. The practical application of this framework would depend on an understanding of the connection between the spraying parameters and the resulting microstructure.

Acknowledgment

This work was supported by NASA through a contract to Tufts University.

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