

Thermal Conductivity of Gelcast Porous Alumina

Larger pores, a compact matrix and smaller fraction of grain boundaries in foams resulted in less effective dissipation of heat transfer and a larger mean free-path for phonons to propagate.

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Intrinsic properties of porous ceramics (e.g., low thermal conductivity, low thermal mass, high permeability and high surface area) along with the high chemical stability of ceramics allow for a wide range of uses.

Thermal insulators constitute one of the major areas of porous ceramics consumption. Measurements of thermal diffusivity and conductivity are important design tools in this field, since temperature variations during heating cycles can be determined and temperature gradients, service temperature and thermal stresses can be assessed.

Because measurements of thermal conductivity are elaborate and laborious, attempts have been made to predict this property using more easily measurable parameters. Several models have been developed to describe the thermal conductivity of porous materials, taking into account the role of temperature, porosity, pore size and conductivity of the solid and of the gas contained in pores.

Microstructural features also are of great importance; e.g., the relative configuration of solid and gas phases, microcracks, impurities, inclusions and grain size.

The fabrication of porous ceramics may be designed to render bodies with different properties. Through numerous techniques, the pore size and its distribution may be varied as desired. For instance, an equal volume fraction of porosity can be incorporated within a ceramic matrix either in the form of nanometer scale pores or as cells in the micron to millimeter range.

Nevertheless, control of processing

parameters must be established, and that may prove to be a difficult task.

This work presents a study of the thermal conductivity of porous bodies processed by two different techniques, thus producing bodies having different pore morphology and pore size distribution.

One approach consisted of foaming ceramic suspensions prior to setting by in situ polymerization. Another method involved dry pressing and bisque firing at various temperatures.

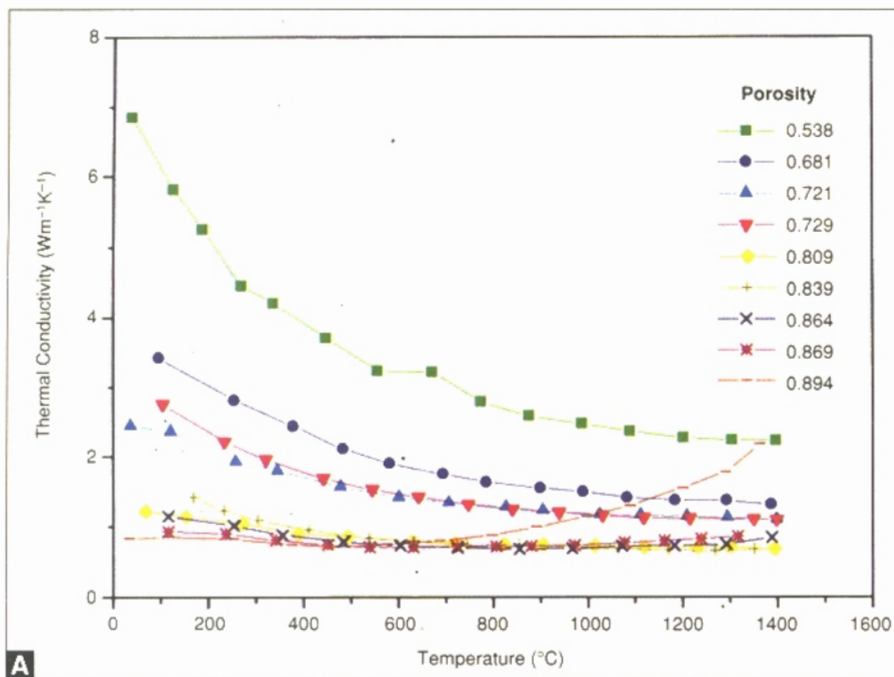
Thermal conductivity data were derived from measurements of diffusivity that was carried out by means of laser-flash technique. The data were evaluated in terms of their dependence on temperature and pore fraction.

Techniques for Porous Ceramics

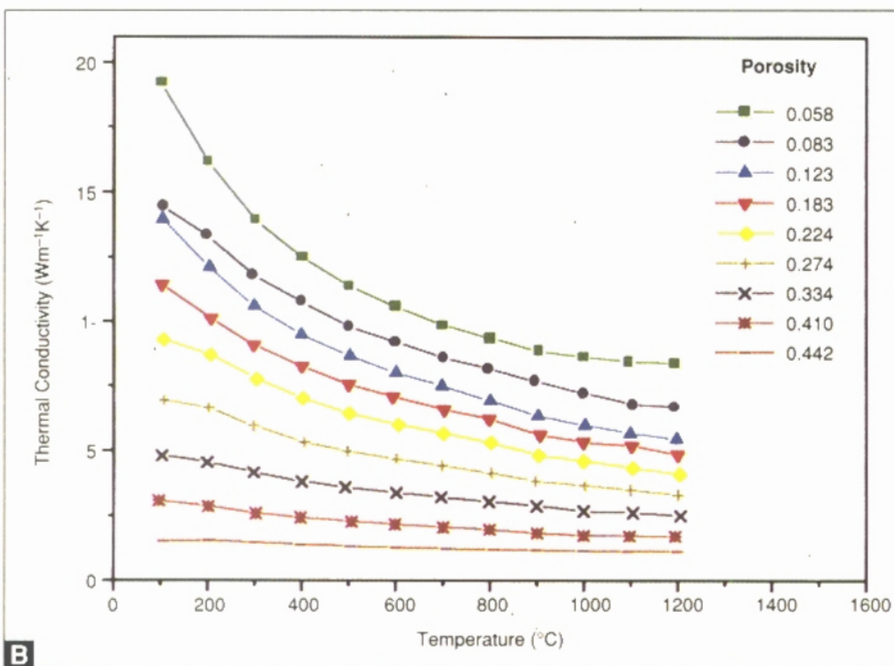
Gelcast ceramic foams were produced according to the procedure previously described by Sepulveda. The process involves the preparation of an aqueous suspension containing ceramic powder, polyelectrolytes as dispersing agents and organic monomers for posterior setting.

Surfactant is added to the ceramic suspension, and mechanical agitation generates a foam. Porosity levels can be varied by raising a fixed amount of suspension to the desired volume in accordance with the surfactant concentration.

Setting of the foamed suspensions is induced by the addition of chemical substances that initiate in situ polymerization of the monomers forming a gel. After



A



B

Thermal conductivity as function of temperature for porous alumina produced through (A) the gelcasting of foams and (B) dry-pressing and sintering at various temperatures.

demolding and drying the liquid, the samples are sufficiently strong to withstand machining.

For thermal conductivity measurements, unsintered samples were cut and designed to have postsintering dimensions of 6–12 mm in diameter and 1 mm in thickness. Sintering was carried out at 1550°C for 3 h to obtain a fully densified ceramic matrix.

Sintered samples with densities ranging from 0.42–1.84 g/cm³ (corresponding to a porosity/volume fraction of 0.538–0.894) were evaluated in terms of their thermal conductivity. Densities <0.42 g/cm³ also were produced. Nevertheless, thermal conductivity measurements of these samples were not possible because a laser can pass straight through the large pores

that characterize such structures.

Foamed ceramics are associated with cellular structures and characterized by: (a) pores that originate from each bubble in a foam, usually named cells; and (b) interfaces between cells that are formed when partial rupture of the foam film takes place, called interconnections. It is difficult to determine which of the two magnitudes is more adequate to characterize the pore structure.

For applications involving permeability properties, the interconnection dimension may be a determinant factor. The latter may have lower significance in uses that require good mechanical properties and insulation to heat, for which cell size and minimum solid areas are more important indicators.

In the present study, the porosity distribution of gelcast foams was quantified with respect to the cell size distribution using an image analyzer. The approach consisted of linear intercept measurements across the cell length on the cross-sectional area of samples with 15 mm diameter, considering a minimum of 800 counts.

Histograms of cell size distributions were plotted and fitted to a Gaussian function. The median and limit values of the distribution were used to represent the cell size of each sample.

The thermal conductivity of porous foams was compared to results previously reported by Santos and Taylor. They used a different approach to processing alumina into porous forms. That process involved dry pressing into disk-shaped compacts for preconsolidation and sintering at various temperatures to alter the porosity level.

Temperatures ranging from 1000–1600°C were employed for 2 h to produce partially sintered microstructures. This procedure resulted in bodies with final densities of 2.22–3.75 g/cm³ (equivalent pore fraction of 0.058–0.442). The pore size distribution of these samples was determined by mercury porosimetry.

Measurements

Preparation of samples for thermal conductivity measurements consisted of coating the sample's surface with

carbon (spraying aerosol colloidal graphite) as a means to improve emissivity.

The thermal diffusivity (α) was measured in vacuum using the heat-pulse technique (Nd-glass laser wavelength 1067 μm) with an InSb infrared detector (UMIST diffusivity apparatus). Temperature in these tests was raised from 100–1400°C. The technique is based on the incidence of a brief (1.5 ms) and uniform heat pulse on the front face of the sample and recording the temperature history on the rear surface.

Considering that heat losses are negligible, the temperature at the rear surface is given by

$$T^* = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \omega^2) \quad (1)$$

T^* is a dimensionless parameter given by the ratio T/T_m , where T and T_m are the instantaneous temperature and the maximum temperature at the rear face, respectively. The dimensionless term ω is defined as $\pi^2 \alpha t/L^2$, where α is the thermal diffusivity, t is the time and L is the specimen thickness.

One way to express the thermal diffusivity for $\omega = 1.38$ is as follows.

$$\alpha = 1.38L^2 / \pi^2 t_{1/2} \quad (2)$$

where $t_{1/2}$ is the time required to raise the temperature of the rear face to half of the maximum temperature rise; i.e., T/T_m is 0.5.

The thermal conductivity λ may be derived from data of thermal diffusivity by using the expression:

$$\lambda = \alpha \rho c_p \quad (3)$$

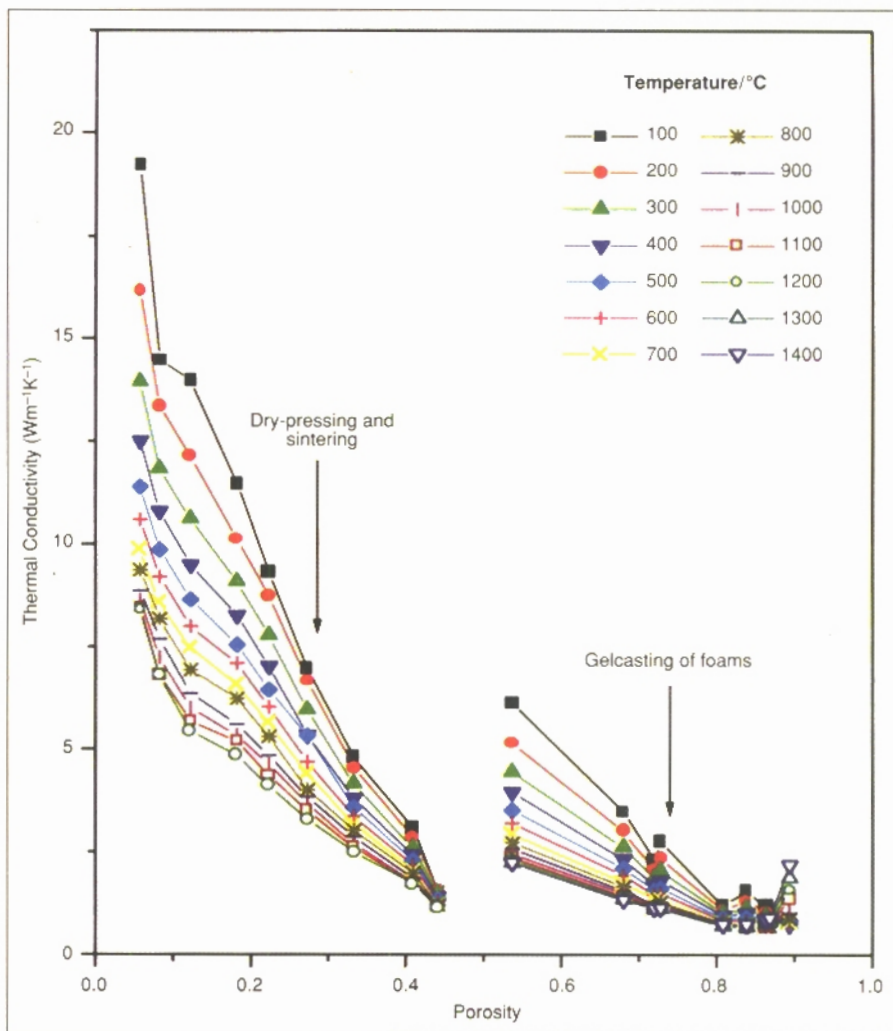
where ρ and c_p are, respectively, the density and specific heat values of alumina.

There are many expressions that describe the specific heat of pure alumina as function of temperature. The equation used here is expressed as:

$$c_p (\text{Jkg}^{-1}\text{K}^{-1}) = 1076 + 0.2249T - 4.432 \cdot 10^{-5} T^2 - 3.322 \cdot 10^7 T^{-2} \quad (4)$$

TC vs. Temperature

Results of thermal conductivity as a function of temperature for gelcast foams were compared to results retrieved from the previous work by Santos and Taylor.



Data of thermal conductivity measured at different temperatures in vacuum for porous alumina produced through gelcasting of foams, and through dry-pressing and sintering at various temperatures.

In general, for dielectric solids above the Debye temperature, thermal conductivity decreases as temperature increases. The following fitting is usually applied.

$$\lambda = (A + BT)^{-1} \quad (5)$$

where A and B are material-dependent constants. A is related to the collective contribution of scattering by all point defects, and B is associated with intrinsic thermal conductivity due to phonon-phonon interactions (Umklapp processes).

Foams with porosity fractions >0.839 displayed a shift in thermal conductivity at temperatures above 600°C. An additional term had to be incorporated into the above equation, as follows:

$$\lambda = (A + BT)^{-1} + CT^3 \quad (6)$$

The term CT^3 accounts for the radiative contribution in heat transport, where C is a constant related to the effects of the refractive index, effective absorption and scattering coefficients of the material.

The values of A , B and C for the fittings applied to the thermal conductivity of foams and of pressed bodies as function of temperature resulted in an R^2 coefficient ~ 1 , which denotes a good correlation.

In porous bodies, contributions of several mechanisms can occasion heat transport, including conduction through solid and gaseous phases, convection in the gaseous phase and radiant heat transfer at high temperatures.

In the present study, experiments were performed in vacuum, therefore, conduction and convection related to the presence of gas were ignored. In practical applications, however, these mechanisms may be present, and it is important to acknowledge their role.

Gas contained in pores usually constitutes a major fraction of the porous component. Despite the fact that gases are classified as poor conductors, they can influence conductivity. Energy can be transferred through the gas medium by molecular interactions in the event of collisions.

Litovský described the influence of gas pressure on the thermal conductivity of porous ceramics. Conductivity increases in accordance with the partial gas pressure, once molecular interactions are more frequent in a less rarefied medium.

Another means of heat transfer by gas refers to convection. Convective motion in porous bodies involves circulation of gas within the small bounds defined by pore walls, usually with diameters <10 mm, and is generally negligible.

In dielectric solids, such as alumina, and at low temperatures, heat transfer is accomplished mainly by propagation of nonharmonic elastic waves in the solid (phonons). It is proportional to the specific heat of the material and to the wave mean free path. The energy dissipation that leads to conductivity decreases, therefore, when thermal activity and lattice vibration increase. This is explained by scattering in phonon-phonon interactions and other anharmonicities that lead to a smaller mean free path.

The observed effect of radiation increasing the thermal conductivity at temperatures >600°C for porous foams containing porosity fractions >0.839 is based on the transfer of heat in the form of higher frequency electromagnetic radiation energy (photon conductivity).

Albeit all bodies above absolute zero temperature radiate energy, the amount of energy emitted increases with the third power of temperature. Only in porous bodies and at high temperatures is the radiation effect observed.

Taking into account intrinsic characteristics of ceramic processing and

aspects of mechanical strength for handling and homogeneity, the two techniques studied here lead to distinct porosity ranges.

Dry pressing was limited to lower pore fractions, while foaming leads mainly to ultrahigh porosity forms. Despite this difference, comparable values of conductivity were obtained within the tested temperature range for both processes.

A case in point includes foams with 0.721–0.729 porosity ($\rho = 1.08 \text{ g/cm}^3$) and dry-pressed bodies containing 0.442 porosity ($\rho = 2.22 \text{ g/cm}^3$), which displayed thermal conductivity of ~1.09 W/mK. In fact, a higher volume fraction of pores has to be incorporated in gelcast foams in order to reach similar levels of conductivity to those attained with dry-pressed bodies.

The insulating characters of bodies processed by both techniques differ basically because of microstructure variations; in particular, the manner in which porosity is distributed within the solid matrix.

TC vs. Porosity

The thermal conductivity data, as function of porosity fraction at various

temperatures, revealed that porosity fraction increments caused a considerable decrease in the thermal conductivity of the ceramic bodies.

A sharper decrease in thermal conductivity occurred when porosity increments were made within the lowest porosity fractions. This decrease became slighter as the volume of enclosed pores increased.

For gelcast alumina foams, when the porosity increased from 0.538 to 0.894, the thermal conductivity was lowered from 6.8 to 0.7 W/mK at room temperature. At the highest temperature tested, the conductivity decreased from 2.2 to 0.7 W/mK and then increased again to ~2.2 W/mK.

In turn, dry pressed samples with 0.058–0.443 porosity exhibited thermal conductivity decreasing from 19.2 to 1.5 W/mK and from 8.4 to 1.1 W/mK at room temperature and at the highest temperature, respectively.

Porous bodies are commonly considered two-phase systems; i.e., solid and gaseous, where the low thermal conductivity of gas is one of the important attributes that describe its component properties.

Even though current experiments refer to the thermal conductivity in the

Correlation Between Thermal Conductivity and Temperature for Gelcast Foams

Density/ g cm ⁻³	Porosity	A/ 10 ⁻¹ m KW ⁻¹	B/ 10 ⁻⁴ m W ⁻¹	C/ 10 ⁻¹⁰ m K ⁻⁴ W ⁻¹	R ²
0.42	0.894	6.157	16.5	3.944	0.982
0.52	0.869	6.922	9.754	1.046	0.953
0.54	0.864	3.657	12.8	0.910	0.987
0.64	0.839	1.393	13.3	0.598	0.989
0.76	0.809	5.388	8.344	0.409	0.991
1.08	0.729	1.050	6.867	0.655	0.999
1.11	0.721	2.288	5.458	0.489	0.993
1.27	0.681	1.101	4.823	0.467	0.997
1.84	0.538	0.487	3.109	0.981	0.997

Correlation Between Thermal Conductivity and Temperature for Dry-Pressed and Sintered Specimens (Santos and Taylor)

Density/ g cm ⁻³	Porosity	A/ 10 ⁻¹ m KW ⁻¹	B/ 10 ⁻⁴ m W ⁻¹	R ²
2.22	0.443	5.270	2.720	0.968
2.35	0.410	2.370	2.540	0.994
2.65	0.334	1.420	1.760	0.998
2.89	0.274	0.854	1.470	0.996
3.09	0.224	0.587	1.240	0.996
3.25	0.183	0.455	1.110	0.998
3.49	0.123	0.321	1.060	0.998
3.65	0.083	0.394	0.780	0.998
3.75	0.058	0.261	0.745	0.978

absence of gas, as noted previously, results show that the inclusion of pores in various distributions within the ceramic structure can significantly alter the overall heat transport.

Upon observing the decrease of thermal conductivity with porosity increase, it can be seen that a discontinuity exists at the point where the processing technique switches from dry pressing to gelcasting of foams. A single trend, therefore, cannot simultaneously describe the variation of conductivity with porosity for both techniques.

These results show that expressions relating heat transport phenomena of porous bodies only to volume fraction of pores and solid may depart from exactitude, since they ignore the effects of microstructure and pore size distribution on the properties. In the same fashion, microstructural effects may explain the differences between foams and presintered bodies in terms of radiation scattering.

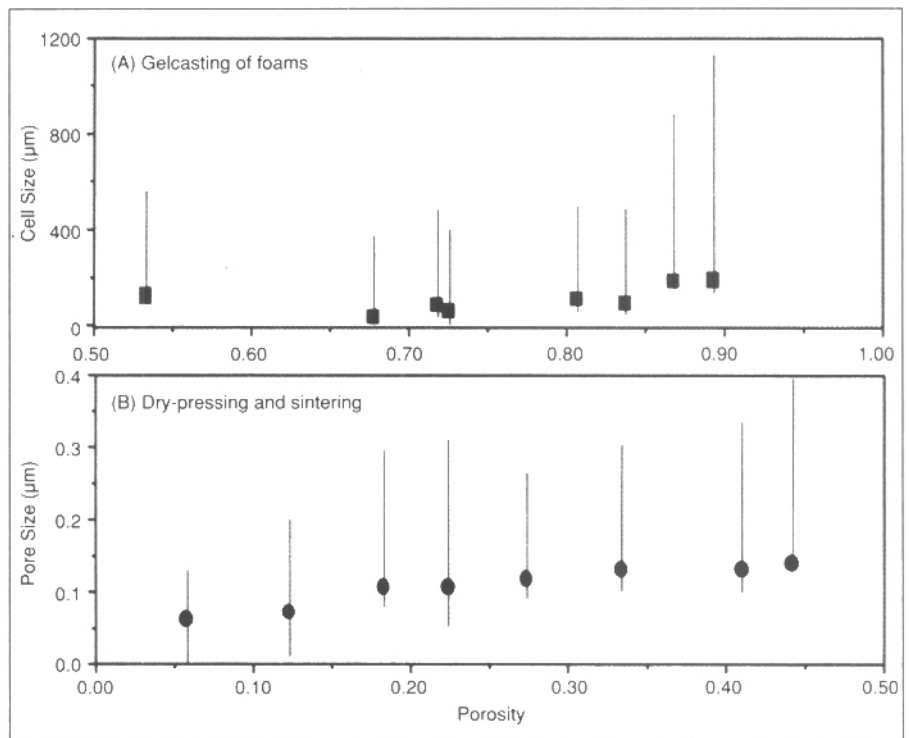
The properties of porous bodies frequently are described as a function of porosity fraction in a single magnitude. Published works depicting the role of pore size, pore shape and size distribution are scarce. Difficulties still remain in establishing reliable magnitudes to describe the porous network, which has intricate shapes and is hardly uniform.

Micrographs of porous alumina manufactured by foaming and by dry pressing and sintering at various temperatures illustrate the differences of pore dimensions and grain size. The microstructures indicate that the surface area of pore boundaries and solid-solid contacts vary considerably from one process to another.

The porosity of bodies measured by image analysis revealed that the size of each cell originated from a bubble in gelcast foams. In dry-pressed bodies, there is an equivalent diameter of inter-granular pores attained by mercury porosimetry.

Foams are formed by cells in the size range of 30–1000 μm , with a median of 50–300 μm . The cell size distribution depends mainly on the specimen density, although other process parameters can be conveniently controlled to alter this range.

The solid matrix in foams is charac-



Pore size of porous alumina produced by different routes. The gelcast foams (A) had the cell size measured by image analysis and pressed specimens (B) were characterized by mercury porosimetry. The bars represent the range of size and the symbols indicate the median value.

terized by a continuous and compact structure of grains in advanced stage of sintering and growth. Other microstructural features that account for thermal properties, such as residual pores, represent only a small portion of the structure in foams.

Pressed bodies, on the other hand, display a typical microstructure of initial sintering stages having micropores in the range of 0.05–0.3 μm , mainly located in intergranular regions.

The denser versions have fewer and smaller inter-granular pores with larger grain size, whereas more porous specimens are characterized almost by individual particles bridged by necks.

Intergranular pores, grain boundaries, impurities, microcracks and lattice imperfections are known thermal resistances that contribute to phonon scattering by giving rise to anharmonicity in phonon propagation. These factors explain why heat scattering is more pronounced and thermal conductivity is, in general, lower in presintered samples when compared to gelcast foams.

When porosity emerges from differ-

ences in sintering conditions, a significantly higher volume fraction of pore-solid boundaries exists. The solid phase consists of bridged particles of a size similar to the original particle size of the powder, or poorly connected grains with a considerable number of two grain junctions.

To the contrary, foams exhibit a highly densified structure with larger and fully-connected grains that offer an enlarged mean free path for phonon propagation.

In addition, the smaller surface fractions of grain boundaries and solid-pore interfaces reduce phonon-phonon scattering. According to Rice, thermal conductivity can be dominated by the minimum solid area normal to the heat flux. This magnitude is equivalent to the area of the neck between particles in presintered materials and to the thickness of the struts between cells in a foam.

In a simplified fashion, one could say that smaller and better dispersed pores in the structure may enhance the thermal insulation mechanisms since they are associated with smaller mini-

imum solid area and, therefore, a greater number of contact resistances.

The increase of constant A with porosity increase indicates that porosity enhances point-defect scattering. This is probably a result of the increase in solid-pore areas and the decrease in the minimum solid area. Two different trends are noted, depending upon the processing technique used. Term B describes scattering by Umklapp processes and increases proportionally to the porosity fraction.

Only one trend can describe the behavior of both types of material, agreeing with the fact that B describes an intrinsic property of the material. This is considered a direct consequence of the reduction in the overall cross-sectional area across which heat can flow.

As noted previously, thermal conductivity increases with temperature increase for foams with porosity >0.839 and at temperatures as low as 600°C . Heat transfer by radiation is usually described as a function of the material's emissivity and is directly proportional to the size of pore.

Radiation can travel freely through

empty space. It can be dissipated by opaque material in its path in boundary regions or scattered when it hits a refractive surface. Finely divided and higher density materials produce more accentuated scattering than coarser and lower density structures.

The large cells that characterize the structure of foams, therefore, do not dissipate as much radiation as the small pores in presintered, pressed samples. This allows for radiation to be more directly transmitted.

Conclusions

Essential characteristics of insulation materials include suitable thermal and mechanical properties, low thermal conductivity and fuel economy during heating cycles. Porous ceramics generally meet most of these criteria and can be successfully produced through numerous techniques.

The properties of porous ceramics not only depend on the porosity volume fraction but also are strongly influenced by the manner in which this is distributed within the body and by corresponding changes in the microstructure.

Measured thermal conductivity of

porous bodies produced by two different procedures showed that larger pores, a compact matrix and smaller fraction of grain boundaries in foams resulted in less effective dissipation of heat transfer and a larger mean free-path for phonons to propagate.

Remarkably higher volumes of porosity in complex-shaped bodies is possible through foaming/gelcasting. This implies ultralow density, low mass and low conductivity. Furthermore, the mechanical strength of gelcast foams is the most advantageous feature of this type of material. This ensures higher reliability.

For instance, flexural strength as high as 26 MPa has been attained for gelcast alumina containing a pore fraction of 0.70. These numbers are significantly higher than the reported values for other types of porous ceramics.

Powder compacts with porosity varying through sintering temperatures are limited to low porosity volumes due to the lower mechanical strength with which these materials are associated.

Low thermal conductivity levels can be achieved with the low porosity volume in these materials. More energy, however, is necessary to raise the temperature of such dense bodies.

Further improvements in the production of low conductivity bodies with high mechanical strength through the gelcasting of foams would be:

- Generation of smaller cell sizes while maintaining low density levels;
- Use of lower thermal conductivity raw materials.

Variation of cell size is possible by controlling a number of variables in the process, such as the shear rate during foam generation, slip viscosity, time for the onset of polymerization and passage of the fluid foam through a sieve with the desired aperture prior to gelation.

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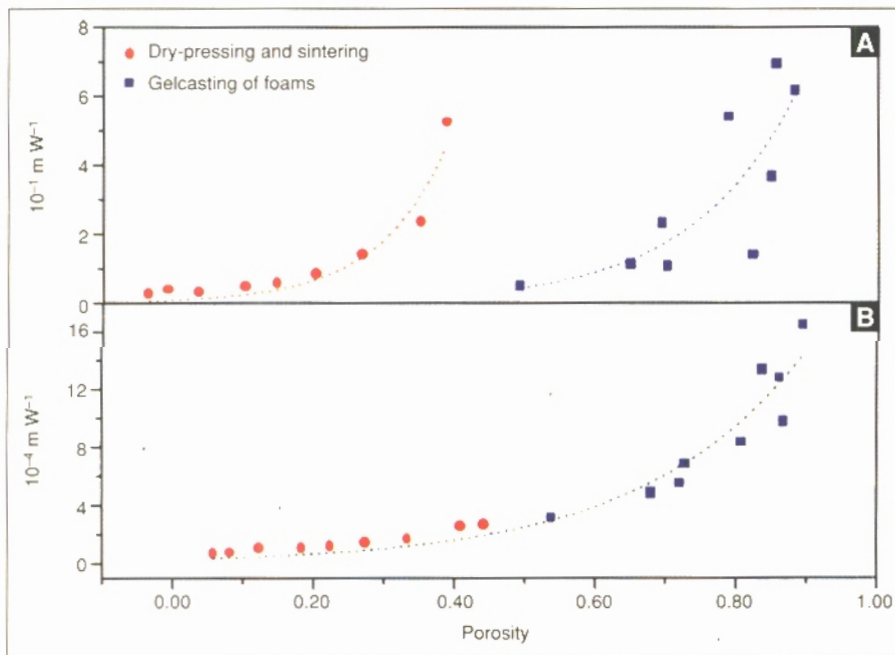


Chart of constants A and B obtained for best fit of equations (5) and (6) to describe the correlation between thermal conductivity and temperature for gelcast foams, and for dry-pressed and sintered specimens. Constant A is related to non phonon-phonon scattering; whereas B is an intrinsic property of the material that is associated with the Umklapp processes (phonon-phonon interaction).

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