THERMAL CONDUCTIVITY OF MICROPARTICLES: CARBON BLACKS AND SOLID SOLUTIONS OF C.B.N.

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Introduction

Small particles of carbon blacks, boron nitrides and (C.B.N.) solid solutions were prepared then investigated as potentially good thermal insulators at high temperatures. Their individual characteristics are reminiscent of the bulk materials but in general they are constituted with crystallites and grains, and a size effect is present. It is therefore necessary to take account of the surface and interface effects and their spatial distribution: the void fraction and the apparent specific weight are the associated usual parameters to introduce an adapted model.

Using a flash method with a short uniform and intense thermal pulse, the thermal diffusivity of the samples has been determined at room temperature. Following an analytical technique the different contributions of the thermal conductivity (solid phase, gas phase and radiations) have been estimated. It allows us to determine the intrinsic thermal conductivity of these submicronic powders.

Summary of the conduction processes

Heat transfer in granular materials is an intricate question; different mechanisms occur both in the solid and gas phases which can interact together at the interfaces.

1) The thermal conduction in the solid as defined by the Fourier's law which is reduced by the boundary scattering of phonons and the resistance contacts between grains.

2) The thermal conduction within the gas; this is the diffusion term as defined by the Fick's law which is mainly pressure dependent [1].

3) The convection process through the pores: the natural convection is negligible with a Raylegh number smaller than unity: this is the case for our samples [2].

4) The radiative heat transfer through the powder. An equivalent radiative conductivity can be defined for a given spectra domain [3]. For carbonaceous materials this contribution is considered as negligible at room temperature. In summary for our type of porous materials, the apparent heat transport coefficient can be expressed by the following expression at a given temperature:

$$\lambda_a = (1-p)\lambda_s + p.\frac{\lambda_g^\circ}{1+\dfrac{\lambda_g^\circ}{L_g.P\sqrt{\dfrac{2R}{\pi MT}}}}.C$$

where p is the porosity factor, λ_s the effective thermal conductivity of the solid phase, λ_g the thermal conductivity of the free gas. P is the pressure, M the gas atomic weight, L_g the characteristic pore size, T the temperature and R the perfect gas constant.

Finally C is an empirical factor which takes account for the interactions between the two processes at the gas-solid interface.

Thermal conductivity measurements

We use a flash method where a short and intense pulse of light is absorbed by the front surface of a disk-shaped cell which contains the investigated powder [4]. Under a controlled pressure, a resulting temperature rises at the rear face as detected by a suitable IR detector. A thermogram giving the normalized temperature variation versus time is recorded which allows us to calculate a thermal diffusion coefficient. To correlate it with the thermal conductivity it is necessary to elaborate a specific model. Considering a three-layer sample under non-adiabatic conditions [5] and following the so-called technique of identification functions [4] the apparent conductivity (λ_a) can be determined from each experimental thermogram. For all the samples for which the chemical preparation is described elsewhere [6] and presented on table 1, we investigate the pressure dependence from atmospheric pressure down to 0.05 mbar. A representative set of results on carbon blacks is presented figure 1. The comparative fits obtained for these submicronic materials allow us to elucidate the following parameters:

i) The influence of both the gas nature and pressure: in particular the apparent conductivity of any powder is very sensitive to the air or helium pressure excepted in presence of a good vacuum.

ii) The influence of the particle size and the porosity. This study concerns the ex-acetylene blacks which present different mean particle sizes (table 1). It appears, for a

quasi constant porosity, that the apparent conductivity measured under vacuum is rather increasing with the particle diameters. The most important fact is the enhancement of this thermal conductivity under atmospheric pressure which is due to the gas phase conduction (for large porosity as indicated by L_g values the convection term could be efficient).

iii) The influence of nanomaterials. Under extrapolation to vacuum it is possible to determine their solid conductivity (λs). The obtained results evidence two classes of compounds: for carbon blacks and boronated carbon a R.T. value as low as 3-4 $mW.K^{-1}.m^{-1}$, but for ternary solid solution and boron nitride a value about 10 $mW.K^{-1}$ m^{-1}. In any case these powders exhibit a thermal conductivity figure which is, at least 10^4 times lower than the expected value for a bulk polycristalline compound [7].

Finally a step further can be accomplished if C is considered as an adjustable parameter. As we observe on table 1, its value is in the range of 1 to 2 for most of the samples excepted for two samples the carbon black N990 and the boron nitride powder. We can conclude that in these cases C would be representative of a thermal interaction between the two phases which depends upon the powder structure and the involved gas-solid interface.

Conclusion

The experimental study on the thermal conductivity of these submicronic particles shows that this flash technique can be adapted for high porosity materials. Under vacuum these materials in natural compaction are very good insulators; the next step would be to carry out the same experiments at high temperatures where the radiation component should be efficient in heat transfer processes.

References

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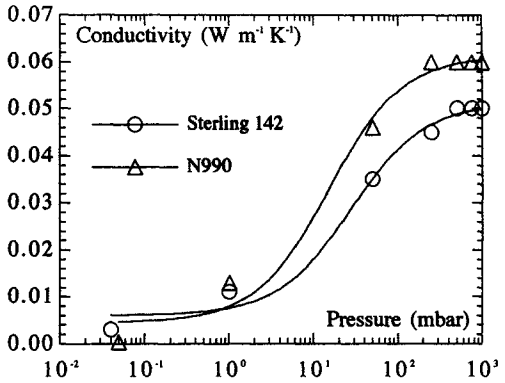

Figure 1

Table 1. Characteristics of the investigated nanomaterials

Samples	Shape and size	Porosity (p)	BET specific area $\tau(m^2g^{-1})$	Apparent conductivity λ_a ($mW.m^{-1}.K^{-1}$)	Lg (μm)	C values
Carbon blacks						
DEGUSSA N990	Spherical (ϕ=200 nm)	0.54	16	3.5	21	4.21
CABOT STERLING 142	Spherical (ϕ=55 nm)	0.82	57	3	11	2.17
SN2A Y70	Spherical (ϕ=40 nm)	0.95	70	4	95	0.77
Binary and ternary compounds						
$C_{93}B_5(O_2)$	Spherical (ϕ=5 nm)	0.96	220	5	3	1.23
$C_{58}B_{18}N_{14}(O_{10})$	Non spherical (ϕ=50 nm)	0.94	50	10	4	1.20
BN	Platelet (thickness 30 nm)	0.68	15	10	13	5.88