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Thermal Conductivity of Compacted AlN Samples

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Abstract

The aim of this work is to obtain, without sintering, AlN compacts with a high thermal conductivity λ. We report in this paper the main experimental results obtained. We show that a high value of λ could not be reached by using only AlN powder. It is necessary to realize AlN/metal binary mixtures to improve the compactness of the samples. Physical aspects such as porosity, ductility of metals and chemical aspects (purity, surface state of AlN powder) must be considered. For AlN–metal compacts, it was considered to be of interest to use the hot-pressing technique in order to reduce porosity by bending metal grains, thus to improving thermal conductivity. Published by Elsevier Science Limited.

1 Introduction

Aluminum nitride is an electrical insulator and an excellent thermal conductor. These properties are especially attractive for many electronic and electric applications, in which thermal dissipation problems could be significant. This material is more suitable than those currently used at present (Al_2O_3, SiC, BeO, ...), because of its high thermal conductivity and its non-toxicity.

Some uses do not allow the sintering of the powder: it is simply pressed by uniaxial or isostatic compaction. The resultant porosity is rather significant, and the thermal conductivity remains much lower than that of a sintered ceramic. Moreover, thermal properties of AlN are very dependent on oxygen content and surface state of the powder.[1,2]

The aim of this study is to develop non-sintered samples, with good thermal properties. For this, two types of samples have been studied: AlN compacts and AlN/metal compacts.

2 Experimental procedure

2.1 Preparation of the samples

Pyrofine® AlN powder (median size 1·5 μm) was used in this study. Several stages were necessary in the elaboration of the samples. Different compounds were added to the aluminum nitride powder: a binder to improve the pressing (phenolic resin, polyvinylpyrrolidone K 15 or polypropylene carbonate), a plasticizer (polyethylene glycol) to facilitate the preparation of the tablet, and a deffloculant (beycostat C213) to favour the homogenization. The mixing was carried out in a liquid medium (absolute ethanol, to avoid AlN hydrolysis). In some cases, a metallic powder (iron, copper or silver) was added, in variable proportions. The mixing took place in a roll mixer for 24 h. The solvent was then eliminated in a rotary evaporator. The samples were compacted with a floating die press. The pressure, comprised between 32 and 112 MPa, was applied for 20 s. The die allows us to obtain a compact with an area of $(4{\cdot}3 \times 2{\cdot}2)\,cm^2$. This first stage of pressing was sometimes followed by a stronger isostatic compaction (200 MPa). Finally, the samples were debinded, to remove the organic compounds.

2.2 Principle of the thermal conductivity measurement

The thermal conductivity is the most well known thermal characteristic and the most used in ceramic materials. It is expressed by the amount of heat which crosses a square meter of a one meter thick material, in unit time, for a difference of one degree between the two opposite surfaces. Fourier's law of conduction gives an expression of the thermal flux density: $\vec{Q} = -\lambda \vec{grad}\ T$, where λ: thermal conductivity ($W\,mK^{-1}$); T: temperature at the considered point.

2.2.1 Experimental device

The aim of the test rig is to establish a constant and uniform thermal flux density across the parallelepiped samples, at steady-state, like that present in an infinite slab edged with two isothermal and uniform slabs, with plane and parallel sides.

This device is called 'hot sheet'. Heating cores (connected up with an alternating voltage generator) and a thermocouple are slipped into a central copper slab called the 'hot component'. Two identical samples are placed on both sides. Other copper sheets, called 'cold components', flank the samples. Screws are used to grip the whole. Inside these two furthest sheets other thermocouples are laid. All these thermocouples allow us to obtain a temperature difference between the cold and the hot component, when steady-state is reached. The device is built symmetrically to avoid a parasitical freak on one side of the hot sheet. Measurements are taken at 100°C, in ambient air. The power given by the generator is $40V \times 0{\cdot}2A = 8\,W$.

2.2.2 Expression of λ

Some simplifying assumptions are admitted:

- convection and radiation losses are negligible;
- conduction is unidirectional;
- tablets/copper contacts are perfect.

The expression of the thermal flux is then given by

$$q = \frac{\lambda}{e} S(T_1 - T_2) = \frac{UI}{2}$$

λ : Thermal conductivity of the sample;
T_1 : Hot component temperature;
T_2 : Cold component temperature;
S : Area of the sample in contact with the hot or cold components;
e : Thickness of the sample, perpendicular to the heat flux;
$P = UI$: Power given by the generator;
$\Delta T = T_1 - T_2$.

Thus, expression of thermal conductivity becomes:

$$\lambda = \frac{UIe}{2S\,\Delta T} (W\,mK^{-1})$$

λ is thus obtained with an experimental error of about 5%.

2.3 Porosity measurements

Mercury porosity cannot be measured because of the size of a sample which is too large for the measurement cell. Because of the non-homogeneity of the sample (edge effects), the result obtained is not representative of the whole. Thus, the density is simply deduced from the dimensions and the weight of the sample. Then, the porosity is calculated from the relation

$$\Phi = 1 - \frac{\rho_{exp}}{\rho_{theo}}$$

ρ_{exp}: Measured density, ρ_{theo}: Theorethical density,

Φ is thus obtained with an experimental error of about 2%.

3 Experiments and Results

The non-sintered samples can be represented in a first approximation by a random packing of spheres. The aim is to optimize thermal transfer across this discontinuous structure. The main factors influencing the thermal conductivity of the compacted samples are porosity and impurities (oxygen in substitution of nitrogen in the crystal lattice, or formation of a superficial hydroxide layer). This problem has two aspects:

- a physical aspect: decreasing the porosity, by increasing the number and the size of the contacts between grains;
- a chemical aspect: acting on the nature of these contacts, and improving thermal transfer across exchange areas.

3.1 Effect of the surface state of the powder

An ageing process occurs. The observed diminution of conductivity with time is certainly caused by the hydrolysis of the powder by contact with ambient air. There is then formation of surface hydroxides, which damage the thermal conductivity. Thus, to solve this problem, the powder is treated, at high temperature (1100°C, 3 h), in a reducing atmosphere. Results are reported in Table 1.

3.2 Effect of the nature and concentration of binder

Several attempts are made to act on the chemical characteristics of AlN samples by using different binders. Phenolic resin produces 30% of carbon residues, PPC (polypropylene carbonate) does not leave any, and PVPK15 (polyvinylpyrrolidone with an intrinsic viscosity of 15) has an intermediate behaviour. Three concentrations are studied for PVPK15. The carbon content is evaluated by a colorimetry technique. The values of the measured conductivities are reported in Fig. 1. These results show that the presence of carbon residues improves the thermal conductivity.

Table 1. Thermal conductivity ($Wm^{-1}K^{-1}$) for compacts prepared with AlN powder treated or not at high temperature under reducing atmosphere

Non-treated powder	$\lambda = 1{\cdot}43$
Treated powder	$\lambda = 1{\cdot}52$

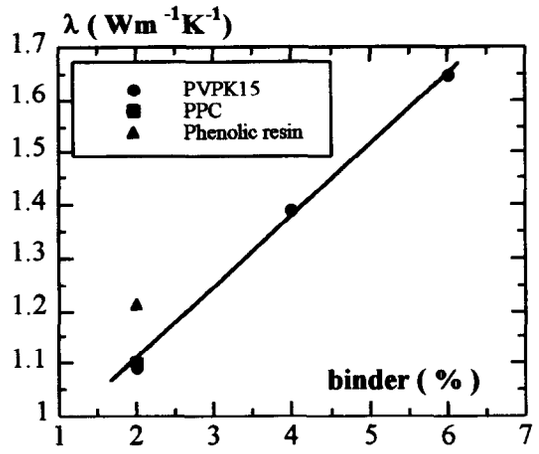

Fig. 1. Effect of the presence of carbon residues on thermal conductivity.

3.3 Effect of the compacting pressure

A series of samples is prepared with a uniaxial press (pressure range between 32 and 112 MPa). Values of porosities and thermal conductivities are represented in Figs 2 and 3. Although the porosity decreases with increasing pressure, it remains high, and the associated conductivities remain insufficient. This can be explained by the fact that AlN is a very hard material, and so the grains do not bend. It is possible to model the rubbing losses between powder and the walls of the die:[3]

$$\frac{Pd_0}{d-d_0} = \frac{d_m}{k\mu(d_m-d_0)} + P\frac{d_0}{d_m-d_0}$$

P : Uniaxial pressure applied (MPa);
d : Density measured at the pressure P;
d_o : Bulk density;
d_m : Maximal density of the pressed sample;

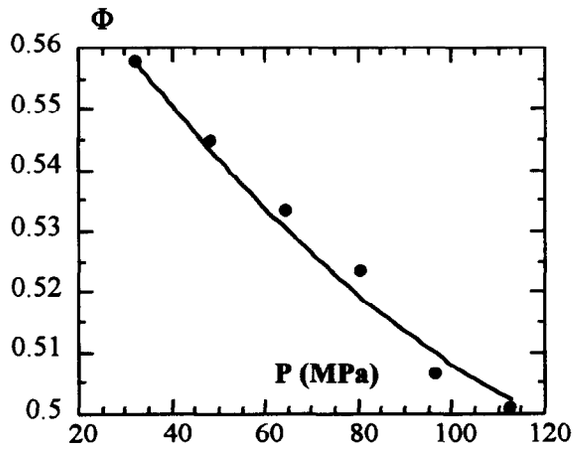

Fig. 2. Effect of uniaxial pressure on the porosity.

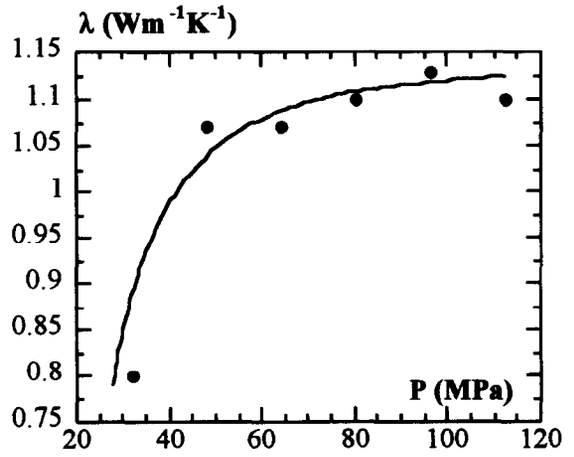

Fig. 3. Effect of uniaxial pressure on the thermal conductivity.

$k\mu$: Characteristic constant of the powder and of the die.

The experimental values agree with this model (Fig. 4) by extrapolation, the minimal porosity that could be reached will be 49%.

3.4 Effect of the use of binary mixtures AlN/metal

Metallic powders are added to the aluminum nitride. First, an iron BASF (median size 4·4 μm) is used (volume fractions range between 0 and 0·38). The compacts are prepared by isostatic pressure of 200 MPa. Results obtained for the porosity Φ and the thermal conductivity λ are reported in Figs 5 and 6. When the iron content increases, there is a decrease in porosity, and a slight improvement of the thermal conductivity. But the sample with 38% of iron is an electrical conductor, and so unusable. Other more ductile metallic powders of different size are also used. In Table 2, the measured values are reported. The samples are pressed uniaxially at 64 MPa.

The addition of a metal with a high thermal conductivity and poorly oxidisable increases the effective thermal conductivity. This evolution can be linked to the properties of binary mixtures: a set

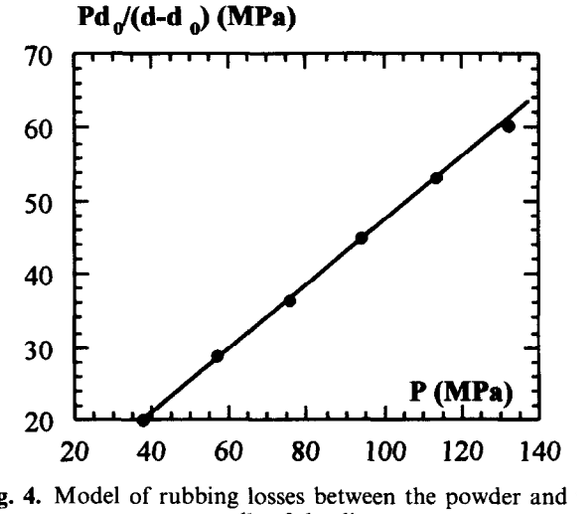

Fig. 4. Model of rubbing losses between the powder and the walls of the die.

Table 2. Thermal conductivity ($Wm^{-1}K^{-1}$) of compacts prepared with various mixtures AlN/metal

% vol metal	AlN	Fe (4·4 μm)	Cu (5·2 μm)	Cu (2·6 μm)	Cu (22 μm)
0	1·2				
25		1·47	2·07	1·75	1·46
30			2·28		1·21
36			2·31		

Table 3. Characteristics of compacts prepared with mixture AlN/Cu 2·6 μm (25%), hot-pressed or not

Experimental conditions	*Porosity*	λ *($Wm^{-1}K^{-1}$)*
T = 880°C P = 32 MPa t = 60 mn	0·43	3·64
T = 20°C P = 32 MPa t = 20 s	0·47	1·75

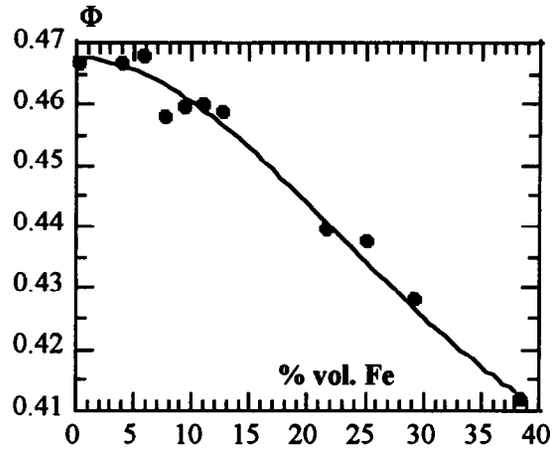

Fig. 5. Effect of iron content on the porosity of AlN/Fe compacts.

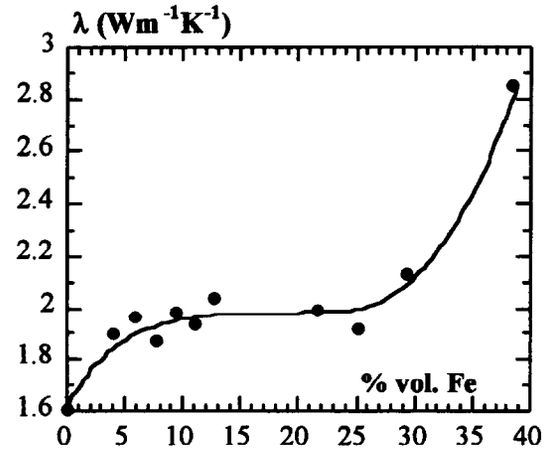

Fig. 6. Effect of iron content on thermal conductivity of AlN/Fe compacts.

of two sizes of grains has a lower porosity than when there is only one size.[4–6] Due to the substitution of several small grains by one big grain, the porous volume decreases. This process allows us to obtain higher values of thermal conductivity with lower porosities.

3.5 Effect of high temperature pressing

Pressings are realized on samples containing copper at a temperature of 880°C. The ductility of the metal is thus improved; experimental results are reported in Table 3. The measured porosity is lower, and so the thermal conductivity is higher. This area must be further investigated.

4 Conclusions

Increasing the value of the compacting pressure is useless because rubbing losses between the powder and the wall of the die lead to harmful heterogeneousness. Metallic additions by cold pressings have no significant effects. Furthermore, the addition of copper and hot pressing seems to be an interesting solution. Even if many precautions are taken, the powder could be in contact with air for a moment. It is then possible to treat the powder at high temperature to decompose surface hydroxides.

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