JOURNAL OF MATERIALS SCIENCE 27 (1992) 3405–3408

Influence of microstructural parameters on thermal diffusivity of aluminium nitride-based ceramics

A. HAFIDI, M. BILLY, J. P. LECOMPTE
Laboratoire de Céramiques Nouvelles, CNRS URA 320, Faculté des Sciences, 123, Avenue A. Thomas, 87060 Limoges Cédex, France

Thermal diffusivity of various AlN-based ceramics obtained by hotpressing or hot isostatic pressing has been measured at room temperature using the laser-flash technique. It is shown that diffusivity: (i) depends on nature and oxygen contents of the starting powders; (ii) decreases with porosity of the materials, especially near to theoretical density; (iii) is strongly influenced by the nature and amount of sintering aids (BeO, MgO, CaO, Y_2O_3 . . .) used for densification, as a result of microstructural effects. For a given additive, the best performances are expected when using firing temperatures which allow the formation of a fairly viscous liquid phase and its subsequent location at triple points of the grain boundaries.

1. Introduction

Electronic systems are demanding greater density and speed, and the subsequent reduction in size of the circuits requires new technologies of multi-layer ceramics and interconnection boards. In such electronic devices, however, the heat dissipation through the substrate needs materials with higher thermal conductivity to avoid chip destruction.

Among them, aluminium nitride has received much interest in the past few years because of remarkable properties, such as a theoretical thermal conductivity (320 $W\,m^{-1}\,K^{-1}$) [1] over 10 times that of alumina (currently the dominant substrate), a high electrical resistivity and low dielectric constant and loss, as well as a thermal expansion coefficient close to that of silicon. All these properties make AlN attractive as a heat spreader in integrated circuits for higher voltage and power electronic devices.

As far as sintered materials are concerned, however, thermal conductivity values ranging from 50 to 260 $W\,m^{-1}\,K^{-1}$ have been reported in the literature [2, 3], instead of 285 $W\,m^{-1}\,K^{-1}$ measured on monocrystals [4]. The reason for such discrepancies are not quite clear, the major obstacle for commercializing AlN, for electronic applications is in fact, apart from its cost, the lack of reproductibility in the conductivity of heat. And it must be expected that this obstacle will last for a long time without a better understanding of the phenomenon.

The present paper is an attempt to tackle this problem of heat conductivity or diffusivity in AlN ceramics and to master its relationship to sintering or microstructural parameters. Purity of the starting powders, porosity of the AlN bodies, nature and amounts of sintering aids used for densification will be examined in succession.

2. Experimental procedure

2.1. Samples preparation

All the starting AlN powders used in this study had been obtained from carbo-thermal reduction of alumina in a flowing nitrogen atmosphere. Their main characteristics reported in Table I only show slight differences between themselves apart from their degree of purity (oxygen and carbon contents).

These as-received powders were hot pressed into 8 mm diameter compacts in a BN coated graphite die under 27 MPa in a nitrogen flow. Temperatures in the range 1600–1800 °C and dwelling times (within one hour) depended on the wanted residual porosity. For achieving fully dense bodies near the theoretical density, hot isostatic pressing (HIP) was also carried out. Then presintered specimens of relative density > 95% were encapsulated in quartz and one hour hot isostatically pressed at 1700 °C under 170 MPa.

In other experiments, AlN powders from Starck Ltd (grade B) were mixed with different amounts of oxide additives, such as BeO, MgO, CaO or Y_2O_3. The conditions in which they were hot pressed, as well as details concerning the sintered specimens (relative densities or nature of the second phases from X-ray analysis) have been specified in Table II.

2.2. Thermal diffusivity measurement

Thermal diffusivity was determined by means of a laser-flash method [5] using a Nd-doped glass laser operating at 1.06 μm with a pulse of 400 ms and a liquid nitrogen cooled In–Sb detector. The pulse energy was 70 J.

Discs of 8 mm in diameter were cut and polished up to about 4 mm thick in order to obtain reproducible and reliable results. Both surface specimens were

0022–2461 © *1992 Chapman & Hall*

TABLE I Main characteristics of the starting AlN powders

Origin	BET specific surface area ($m^2 g^{-1}$)	Mean grain size (μm) BET (calculated)	Mean grain size (μm) Observed	Elemental composition (wt %) Al	N	O	C
Kocht-Light	2.7	0.68	9.0	64.0	33.0	2.7	0.3
Starck (gr. B)	4.4	0.42	4.0	64.8	33.2	2.2	0.5
Atochem	3.5	0.52	1.5	66.1	33.0	1.2	0.25
Tokuyama soda	3.5	0.52	1.5	66.0	33.8	0.6	0.04

TABLE II Sintering conditions of AlN powders (Starck, grade B) with different additives and specifications of the specimens (relative density and crystalline phases at grain boundaries)

Additives (wt %)		1	2	4	4.5	6	8	10	12	15
BeO	Relative density (%)	98.5	98	98		97		99		100
	Sintering conditions			1600 °C, 45 min				1650 °C, 45 min		1700 °C, 45 min
	2nd phases				$BeAl_2O_4$					$BeAl_2O_4$-BeO
MgO	Relative density (%)		99	99		99		98	99	
	Sintering conditions		1780 °C, 90 min				1780 °C, 60 min			
	2nd phases					$MgAl_2O_4$				
CaO	Relative density (%)	97	99	97.5		97	97	97		
	Sintering conditions			1650 °C, 60 min				1650 °C, 40 min		
	2nd phases		CA_2–CA_6		CA–$C_{12}A_7$		CA–C_3A C_3A_5	C_3A_5–$C_{12}A_7$		
CaO	Relative density (%)		98			99		99		99
	Sintering conditions		1500 °C, 150 min			1500 °C, 150 min		1500 °C, 135 min		1500 °C, 120 min
	2nd phases		CA_2–CA_6			$C_{12}A_7$–CA C_5A_3		$C_{12}A_7$–C_5A_3 C_3A		$C_{12}A_7$–C_3A C_5A_3–CaO
Y_2O_3	Relative density (%)	99	100	100	100	100	100	99.4	96	94
	Sintering conditions					1780 °C, 40 min				1780 °C, 30 min
	2nd phases		Y_3A_5				$Y_3A_5 + Y_2A$			Y_2A + Y_2O_3

coated with carbon to assure complete absorption of the flash and avoid laser shine-through. The thermal diffusivity, a, was deduced from the Parker equation [6]

$$a = 0.1388\, e^2/t_{0.5}$$

where $t_{0.5}$ (s) is the time required for the back surface to reach half the maximum temperature value and e (cm) is the sample thickness. Thermal losses were expressed according to the Heckman model [7].

3. Results

3.1. Influence of oxygen contents

AlN powders from different origins (Table I) and containing oxygen contents in the range 0.6–2.7 wt % were hot pressed for one hour, at 1700 °C, without any sintering aid. Our results, which are illustrated in Fig. 1, show that thermal diffusivity steadily decreases with increasing oxygen contents of the starting powders. On the other hand, there are apparently no significant changes in thermal diffusivity as far as carbon impurity content is concerned.

3.2. Influence of porosity

It was investigated on the basis of AlN powders from Starck (grade B) hot pressed or hot isostatically

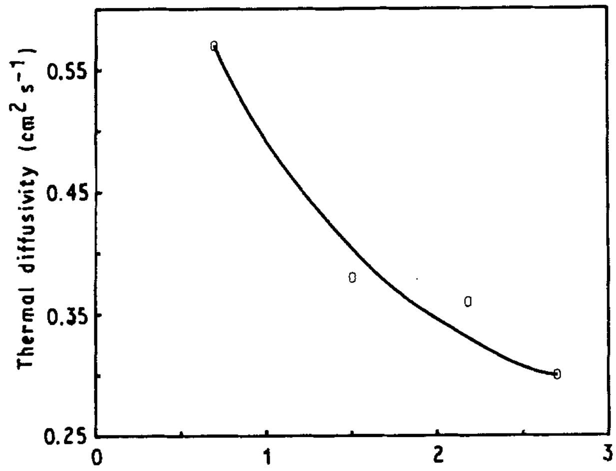

Figure 1 Thermal diffusivity of AlN hot pressed without sintering aid as a function of oxygen contents of the starting powders (each point corresponds to an average of 8 experimental values).

pressed without additive in the conditions already mentioned above. As shown in Fig. 2, there is a sharp decrease in thermal diffusivity in the region of nearly theoretical density ($d > 99.6\%$), followed by values which remain almost constant all along the region of closed porosity (up to 4%) and decrease again when open pores begin to occur.

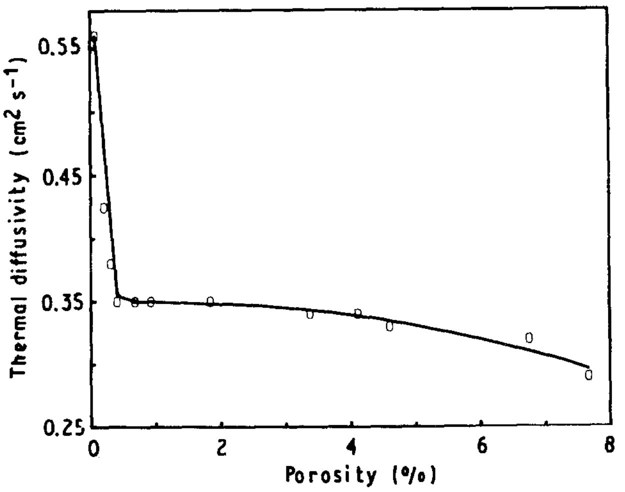

Figure 2 Thermal diffusivity dependence on porosity of AlN from as-received Starck powders.

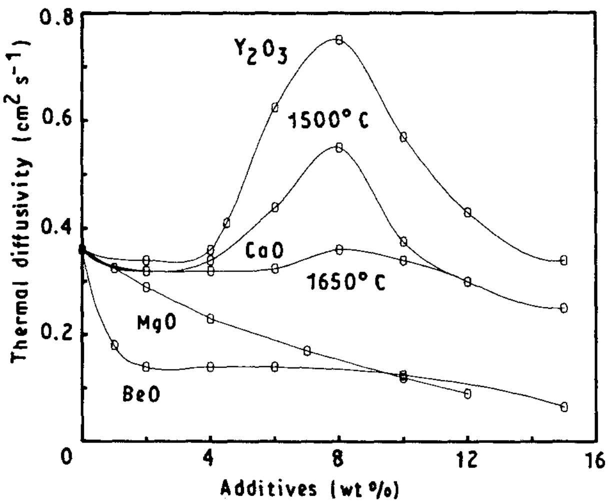

Figure 3 Influence of the nature and amounts of oxide additives on thermal diffusivity (Starck AlN powders).

3.3. Influence of additives

The influence of the nature and amounts of oxide additives for densification is reported in Fig. 3 from specimens of a same porosity (about 1%) whose characteristics are specified in Table II.

In all cases, one can see that thermal diffusivity diminishes with slight amounts of additives but the amplitude of the phenomenon is deeply influenced by the nature of these additives. For BeO and MgO, thermal diffusivity continuously decreases with increasing contents, while maximum values are observed round about 8 wt % in the case of Y_2O_3 and that of CaO, especially when specimens have been sintered at lower temperatures.

4. Discussion and conclusion

The above results first show that thermal diffusivity of AlN-based ceramics is dependent on oxygen contents of the original powders used for densification (Fig. 1). Such a phenomenon has been reported elsewhere in the literature [2]. It can be explained by the fact that superficial alumina which is invariably present on the surface of AlN particles allows the formation of the spinel γ AlON phase [8] in the sintering conditions ($T > 1700\,°C$) of the as-received powders. This second phase, whose thermal conductivity is roughly similar to that of alumina, clearly plays the role of a thermal diffusivity barrier at grain boundaries. As a consequence, there is a negative correlation between thermal diffusivity and amounts of the so-formed AlON and thus of oxygen contained in the starting powders. The high theoretical conductivity value for pure AlN suggest a drastic change in thermal diffusivity in the region of very low oxygen contents, but these concentration levels are virtually impossible to obtain as AlON (and therefore oxygen) is necessary for achieving AlN sintering.

The effect of some oxide sintering aids on thermal diffusivity may be explained in this way. BeO and MgO, for example, also result in lowering diffusivity with increasing oxide contents (Fig. 3), since the spinel phases $BeAl_2O_4$ and $MgAl_2O_4$, which are produced, respectively, play the role of a thermal conductivity barrier at grain boundaries. $BeAl_2O_4$, however, being more fusible than $MgAl_2O_4$, leads to a better wetting of the nitride particles and thus to a sharper decrease in thermal diffusivity for low level contents.

The effect on diffusivity is quite different as far as yttria is concerned as an additive for densification (Fig. 3). It was found indeed that 6–8 wt% Y_2O_3 yielded a maximum diffusivity with declining values on either side of that maximum. The difference in behaviour of such materials cannot only be explained by a higher diffusivity for the yttrium aluminates which, moreover, is about the same as those of the above spinel phases [9]. The only explanation is to be found in more refractory compounds with a more viscous liquid phase at sintering temperatures. It results in secondary phases especially located at the triple junctions of the grain boundaries, which cannot assure a continuous thermal conductivity barrier between AlN particles. This suggests that the maximum diffusivity value must be closely related to a microstructural effect.

Such a point of view is confirmed by the results obtained in the case of CaO additives. When sintering is performed at 1650 °C, calcium aluminates such as C_3A (that is $3\,CaO \cdot Al_2O_3$), $C_{12}A_7$ or CA are formed which remain fluid at this temperature. Their even distribution at grain boundaries has a strong phonon scattering effect. Now, by decreasing the sintering temperature to 1500 °C, there are lesser volume fractions of liquid phase and its higher viscosity prevents a good wetting of the AlN grains from occurring. The second phases are then concentrated at triple points, which leads to a maximum diffusivity value similar to that observed for Y_2O_3. Such a microstructural effect can be extended to other additives, CeO_2 in particular, by a judicious choice of sintering parameters like temperature and oxide contents.

Porosity, has been shown to play an important role on phonon scattering [10]. But the removal of the last traces of porosity produces, in fact, an unexpected effect on thermal diffusivity (Fig. 2). This suggests that the HIP treatment has a beneficial influence on the microstructural distribution of the second phases. In these conditions, much better performances must be expected from adequate compositions such as Y_2O_3 containing AlN, when subjected to a post-sintering HIP treatment.

References

1. G. A. SLACK, *J. Phys. Chem. Sol.* **34** (1973) 321.
2. Y. KUROKAWA, K. UTSUMI and H. TAKAMIZAWA, *J. Amer. Ceram. Soc.* **71** (1988) 588.
3. A. V. VIRKAR, T. BARRET JACKSON and A. C. RAYMOND, *ibid.* **72** (1989) 2031.
4. G. A. SLACK, R. A. TANZILLI, R. O. POHL and J. W. WANDERSANDE, *J. Phys. Chem. Sol.* **48** (1987) 641.
5. F. GITZHOFFER, E. MARIAGE, O. ARBOUCH, G. DELLUC, C. MARTIN and P. FAUCHAIS, Annual Societé Française des Thermiciens Meeting, Limoges, 1988, CPM 12-1 (Societé Française des Thermiciens, 3, rue Heri Heine, 75016, Paris).
6. N. J. PARKER, R. J. JENKINS, C. P. BUTLER and G. L. ABBOT, *J. Appl. Phys.* **32** (1961) 1679.
7. R. C. HECKMAN, *ibid.* **44** (1973) 1455.
8. G. ADO, D. BERNACHE, M. BILLY, K. S. HAN and P. LEFORT, *Rev. Chim. Min.* **22** (1985) 473.
9. G. A. SLACK and D. W. OLIVER, *Phys. Rev. B.* **4** (1971) 592.
10. B. SCHULZ, *High Temp. High Press.* **13** (1981) 649.

Received 20 February
and accepted 20 June 1991