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Hot-pressing of MgSiN₂ ceramics

H. T. HINTZEN, P. SWAANEN, R. METSELAAR

Eindhoven University of Technology, Centre for Technical Ceramics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

W. A. GROEN, M. J. KRAAN

Philips Research Laboratories, P.O. Box 80000, 5600 JA Eindhoven, The Netherlands

In a previous paper it was reported that MgSiN₂ is a promising ceramic material with attractive properties [1]. The most important properties are the high fracture strength, fracture toughness and hardness, whereas the thermal conductivity was measured to be about 17 W/m K. This value is a factor 10 lower than that of AlN [2], but already comparable with that of optimized Al₂O₃ [3]. A considerable improvement may be expected from an optimization of the preparation and processing procedure. First, the MgSiN₂ powder used in the aforementioned study suffers from a high oxygen content. Secondly, the sintering method, using sealed Mo containers to prevent the evaporation of magnesium, is very troublesome and has not led to full density.

The primary aim of the present study was to find a more suitable way of sintering MgSiN₂ ceramics. Here we report on the application of the hot-pressing method to prepare MgSiN₂ ceramics. As the starting material, the same MgSiN₂ powder was used as in the previous study. This MgSiN₂ powder was prepared from Mg₃N₂ (Cerac, 99.9%) and amorphous Si₃N₄ (Sylvania SN402). Further details about the powder preparation can be found in [1]. The hot-pressing experiments were performed in a hot-press model HP20 of Thermal Technology Ind., using an Astro furnace model 100-4560-FP provided with graphite heating elements. The temperature was measured with a thermocouple. The MgSiN₂ starting powder was placed in a graphite die (diameter = 33.7 mm), separated by several graphite

foils impregnated with boron nitride powder in order to obtain several tablets in one run, and closed with a graphite punch. The sintering was performed at a top temperature of 1550 °C and a pressure of 75 MPa for 2 h. The heating and cooling rates were 10 °C/min. Throughout the whole process the furnace was purged with nitrogen.

The density of the MgSiN₂ tablets thus obtained, as measured using the Archimedes method in water, was 3.161 ± 0.002 g/cm³. Compared with the density of 3.11 g/cm³ obtained with the previous method [1], about 2% progress was achieved with the hot-pressing procedure. The density measured in the case of the hot-pressed samples surpasses the theoretical density which can be calculated from the lattice parameters published in the literature (Table I). We therefore measured the X-ray diffraction pattern of the starting MgSiN₂ powder using CuK_α radiation. The lattice parameters were calculated using the *d*-values of the 10 strongest reflections. As a check, the same calculation procedure was applied to the list of *d*-values of [7] and [8] (Table I). The agreement between the published [7] and calculated lattice parameters (Table I) is good. The results obtained in this way for the powder used in the present study are *a* = 0.5256 nm, *b* = 0.6446 nm and *c* = 0.4970 nm (Table I). Without considering the possible influence of secondary phases, this corresponds with a theoretical density of 3.173 g/cm³ (Table I). With respect to this value, the relative density of the hot-pressed MgSiN₂ tablets is about

TABLE I X-ray diffraction data of MgSiN₂ and theoretical density calculated from these data

Lattice parameters			Theoretical density (g/cm ³)	Reference
<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)		
0.5282	0.6474	0.4991	3.130	[1 ^a]
0.5266	0.6472	0.4983	3.145	[1 ^b]
0.5279	0.6476	0.4992	3.130	[4]
0.5272	0.6482	0.4980	3.139	[5]
0.5275	0.6455	0.4978	3.151	[6]
0.5279	0.6476	0.4992	3.130	[7]
0.5284 ^c	0.6477 ^c	0.4991 ^c	3.127	This work
0.5277 ^d	0.6452 ^d	0.4982 ^d	3.149	This work
0.5256	0.6446	0.4970	3.173	This work

^aPowder

^bCeramic

^cCalculated using the *d*-values of [7]

^dCalculated using the *d*-values of [8]

$99.6 \pm 0.1\%$, indicating that full densification is nearly reached. The almost total absence of porosity is demonstrated by the SEM photograph of a fracture surface (Fig. 1). Compared with the MgSiN_2 ceramic obtained in the previous way, the microstructure of the hot-pressed tablets is more uniform, with regular grains of maximum size $1\ \mu\text{m}$.

As indicated by the density measurements and SEM photographs, the thermal contact between the grains seems to be good. The thermal conductivity of the hot-pressed MgSiN_2 samples, determined using a photo-flash method in the same way as described in [1], was $15\ \text{W/m K}$. This is comparable with the thermal conductivity of $17\ \text{W/m K}$ determined for the MgSiN_2 ceramic, processed in the previously described laborious way [1]. Despite a higher density obtained in this work for the MgSiN_2 ceramic, the thermal conductivity was not increased, contrary to expectations [9]. Obviously, other factors play a limiting role, for example the presence of oxygen, as shown for AlN [10]. The oxygen and nitrogen content of the hot-pressed MgSiN_2 ceramic, as determined with a Leco TC 436 O_2/N_2 analyser, were measured to be 4.7 ± 0.2 and $30.7 \pm 1.5\ \text{wt}\%$, respectively. The values are close to those analysed for the MgSiN_2 powder, which was used as the starting material (4.5 ± 0.2 and $30.6 \pm 1.5\ \text{wt}\%$, respectively). This indicates that the oxygen content remains the same during sintering despite the low oxygen pressure as caused by the presence of graphite in the hot-pressing furnace. The presence of oxygen in MgSiN_2 thus originates from the oxygen content of the starting materials. It may result in

oxygen-containing secondary phases, such as Mg_2SiO_4 [1]. When these secondary phases are present in between the MgSiN_2 grains, the thermal contact may be poor and as a consequence the thermal conductivity of the MgSiN_2 ceramic will be decreased.

The incorporation of oxygen in the MgSiN_2 bulk material may be even more detrimental because of phonon-defect scattering. It is known that reduction of the oxygen concentration in AlN by a factor of 9 can increase the thermal conductivity by a factor $\sqrt[3]{9} = 3$ [10]. If this behaviour is also valid for MgSiN_2 , a significant increase in thermal conductivity can be envisaged by lowering the oxygen content.

From the preceding discussion it follows that MgSiN_2 can become an attractive substrate material if the thermal conductivity is further increased. In that case, possible advantages with respect to AlN are the lower processing temperature and possibly lower material costs, combined with a less expansive processing route. To be a suitable substrate material, the electrical conductivity should also be low. The electric resistivity, as measured with a Keithly 617 electrometer, was larger than $10^2\ \text{ohm cm}$ at room temperature. This room-temperature value is comparable with that of AlN [2], and thus appropriate for application of the material as substrates. The high-temperature electric resistivity of MgSiN_2 may be higher than that of AlN [11].

In conclusion, it can be stated that hot-pressing is an attractive technique for preparing almost fully dense MgSiN_2 ceramics, rendering superfluous the laborious route in which closed Mo containers are

Figure 1 SEM photographs of a fractured surface.

applied. Work is in progress to develop a preparation and processing procedure for MgSiN_2 ceramics which yields optimum properties, combined with a fundamental study of the relationship between properties and microstructure.

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