PROCESSING AND CHARACTERIZATION OF AlN-MgO-$MgAl_2O_4$ COMPOSITES BY SPONTANEOUS INFILTRATION

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ABSTRACT

AlN-based ceramic composite using spontaneous infiltration of magnesium alloy into the non-sintered AlN preform at low temperatures (650°C, 800°C, and 950°C) has been fabricated. Microstructural, phase, and chemical analysis show that AlN-MgO-$MgAl_2O_4$ ceramic composites can be made successfully by in-situ reaction of Mg alloy into an aluminum nitride preform under N_2 atmosphere. Electrical conductivity results show that the samples fabricated at 800°C and 950°C are insulators. Thermal diffusivity and heat capacity have been measured using nano-flash and differential scanning calorimetry techniques, respectively. Thermal conductivity results are strongly influenced by the residual porosity. The maximum thermal conductivity value of 95.88 W/m.K was achieved for samples infiltrated at 950°C for 135 min holding time.

INTRODUCTION

Aluminum nitride and its composites are often cited as a potential substrate material for electronic industries due to some unique properties such as high thermal conductivity and low dielectric constant. The idea behind using high thermal conductivity substrates is due to dissipation of heat through the substrate material with the advantage of not using external cooling facilities. Therefore, the demand for high thermal conductivity materials to develop high density integrated packages has increased [1,2]. In order to ensure reliability and efficiency of electronic devices, management of thermal dissipation and thermal expansion matching in electronic substrates is required.

The purpose of the present work is to fabricate non-sintered, AlN-based composites by spontaneous infiltration of molten magnesium alloy (AZ91E) at relatively low temperatures (650-950°C) in order to achieve a dense composite with appropriate thermal properties comparable to that of sintered aluminum nitride ceramic. The theoretical thermal conductivity of single crystal AlN is estimated to be 320 W/m.K [1,3], however the maximum thermal conductivity of polycrystalline AlN has been reported as 272 W/m.K sintered at 1900°C for 100 hours under nitrogen gas [4]. The presence of impurities such as oxygen, which remains either from incomplete conversion of Al_2O_3 or crude processing, reduces the thermal conductivity of the polycrystalline AlN. Table 2.1 summarises the different values of AlN thermal conductivity reported in the literatures. Results show that the sintering process involves high temperature and long times. Therefore, it is an expensive material.

Table 1- Thermal conductivity of aluminum nitride

Thermal Conductivity of AlN at room Temperature (W/m.K)	Additives	Remark	Reference
160-270	Y_2O_3	Sintering at 1750°C -1950°C (1h)	[2]
272	Y_2O_3	Sintering at 1900°C (100 h) under Nitrogen atmosphere	[4]
160	No additives	Hot pressing at 1800°C	. [6]
155	Y_2O_3	Hot pressing at 1900°C	[7]
245	Y_2O_3	Sintering at 1850°C (30 min.) and annealing at 1850°C (100 h)	[8]
114-194	SiO_2 and Y_2O_3 CaO	Sintering at 1825-1860°C (1 h)	[9,10]
175	$CaO.Al_2O_3$	Sintering at 1800°C (1h) under nitrogen atmosphere	[11]
180	Y_2O_3	Sintering 1500ºC to 1900ºC (1h)	[12]

The combination of the thermal properties of the AlN ceramic with the advantages of magnesium and magnesium alloys such as low melting point and high affinity for oxygen, make this combination attractive for sintering applications at low temperature (<1000ºC). Fabricating AlN, MgO, $MgAl_2O_4$ composites at low temperatures (<1000ºC) with reactive infiltration of molten magnesium into non-sintered AlN powder in order to achieve high thermal conductivity could not be found in the literature.

EXPERIMENTAL PROCEDURE

All experiments used AlN powder with 4-5 microns average particle size (dry-pressable grade, supplied by Accumet Materials Co.). It contains 5 wt. % Yttria, 1 wt.% Oxygen, 0.08 wt.% Carbon, 50 ppm Iron, 40 ppm Silicon and 80 ppm other impurities. AZ91E as magnesium alloy was employed for infiltration. Cylinder compacts of non-sintered AlN were prepared by hydraulic force to form preform discs about 1 inch diameter. Magnesium alloys and AlN preforms were placed in a boron nitride crucible and surrounded by a powder bed of AlN in order to facilitate removal of the composite and residual metal

after the experiment. To evacuate oxygen a cylindrical iron chamber and relevant pipes to introduce nitrogen gas (about 1 cm^3/min.) surrounded the BN crucible. In order to achieve full infiltration, simultaneous downward and upward infiltrations have been employed. The boron nitride crucible containing the aluminum nitride preform and two pieces of magnesium alloy (AZ91E), on the top and bottom of the preform, were carefully placed in the furnace (Figure 1). Experiments were performed at three temperatures (650ºC, 800ºC, and 950°C) for different times (25, 60, 90, and 135 min.).

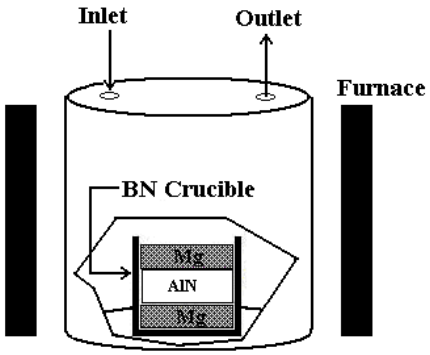

Figure 1- Schematic set-up for upward and downward infiltration of two pieces Mg alloys into AlN preform inside the BN crucible

Infiltrated polished samples were examined using SEM (JEOL JSM-840A) and EDS analysis. Phase identification was performed by X-ray diffractometer (APD 1700, Philips). The Agilent 4339B high-resistance measurements was used at room temperature. In order to calculate thermal conductivity of samples, measurement of thermal diffusivity and heat capacity were made using laser nano-flash (NETZSCH, LFA447) and differential scanning calorimetry (TAinstruments-Q10), respectively.

RESULTS AND DISCUSSION

Morphology and Microstructure Analysis

Samples infiltrated at relatively high temperatures and high holding times have fewer pores and cracks. Figure 2 shows SEM micrograph of polished samples infiltrated at 650°C, 800°C, and 950°C. The EDS patterns show that the dark regions in all samples are composed of aluminum and nitrogen. In samples infiltrated at 650°C, metallic phases such as magnesium, aluminum, and gamma-phase have been detected in bright spots. Therefore, the existence of metals in the final composite indicates incomplete oxidation and nitridation and the ceramic matrix composite formed is unsuitable for electronic applications. In samples infiltrated at 800°C and 950°C, no un-reacted metal has been observed and bright spots have been distinguished as magnesium oxide and spinel ($MgAl_2O_4$) phase by the EDS patterns and XRD results (Figures 3). The XRD results are consistent with the EDS patterns. Yttrium appeared in the analysis of some spots, because the AlN powder contained some yttria. In samples infiltrated at 650°C, The XRD peaks of aluminum and magnesium are detected at all holding times. Gamma-phase ($Mg_{17}Al_{12}$) peaks have been observed only in samples with holding times of 90, and 135 min. However, these peaks are not as strong as those of aluminum and magnesium.

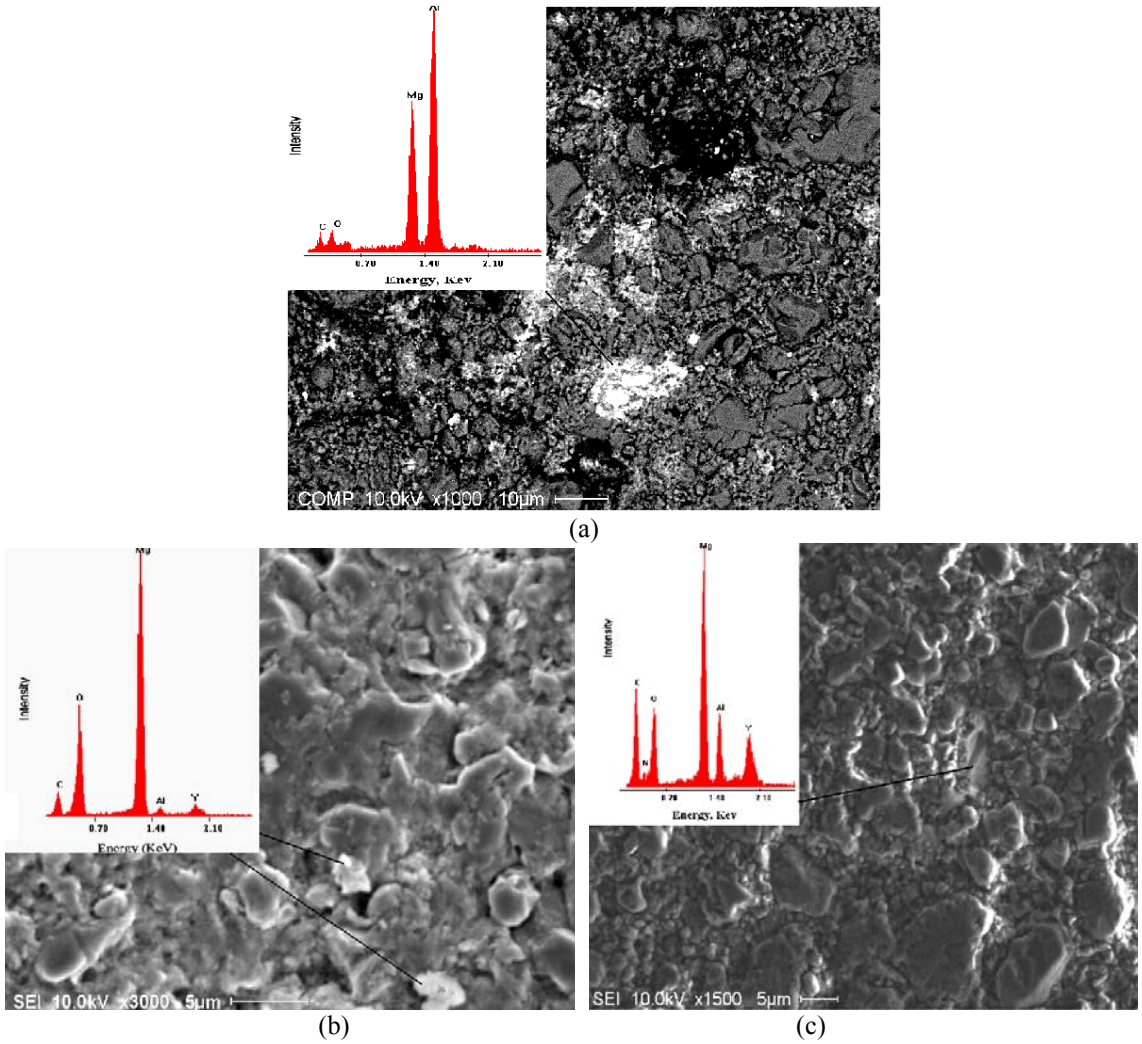

Figure 2- SEM micrographs of samples infiltrated at: a) 650°C with 135 min, b) 800°C with 90 min, c) 950°C with 135 min

The effects of holding time on the phase contents were investigated by the peak ratio technique. The results are shown in Figure 6. The peak ratio is defined as:

$$(I_{hkl} / I_t) \times 100 \quad (1)$$

Where I is XRD intensity and I_t is:

$$I_t = I_{100}\, AlN + I_{200}\, MgO + I_{321}\, Mg_{17}Al_{12} + I_{104}\, Y_2O_3 + I_{111}\, Al + I_{103}\, Mg \quad (2)$$

I_{hkl} is the highest peak for each phase in a given XRD pattern.

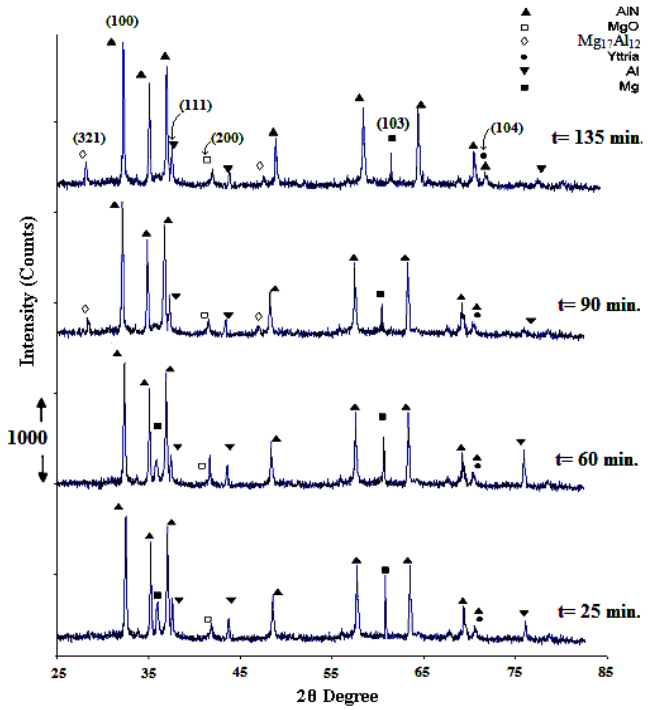

Figure 3- XRD patterns for infiltration at 650ºC with different holding times

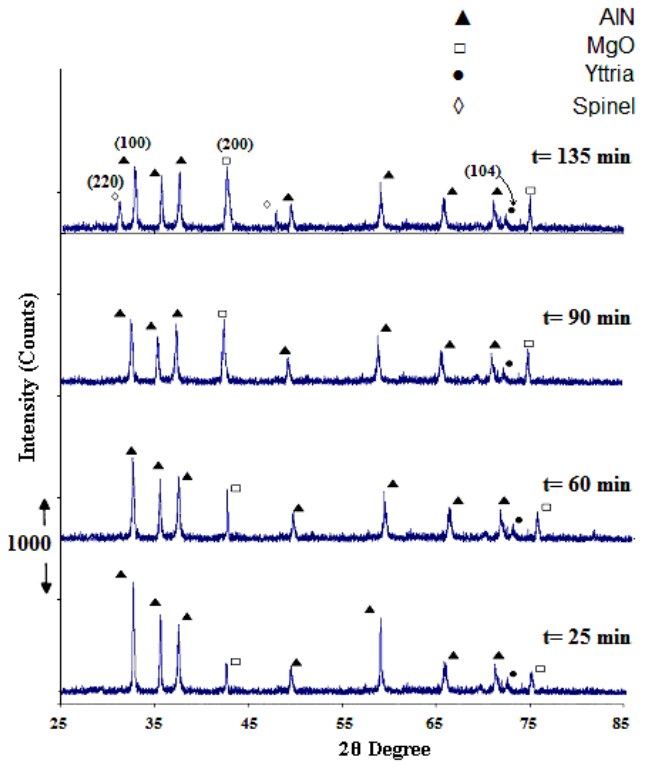

Figure 4- XRD patterns for infiltration at 800ºC with different holding times

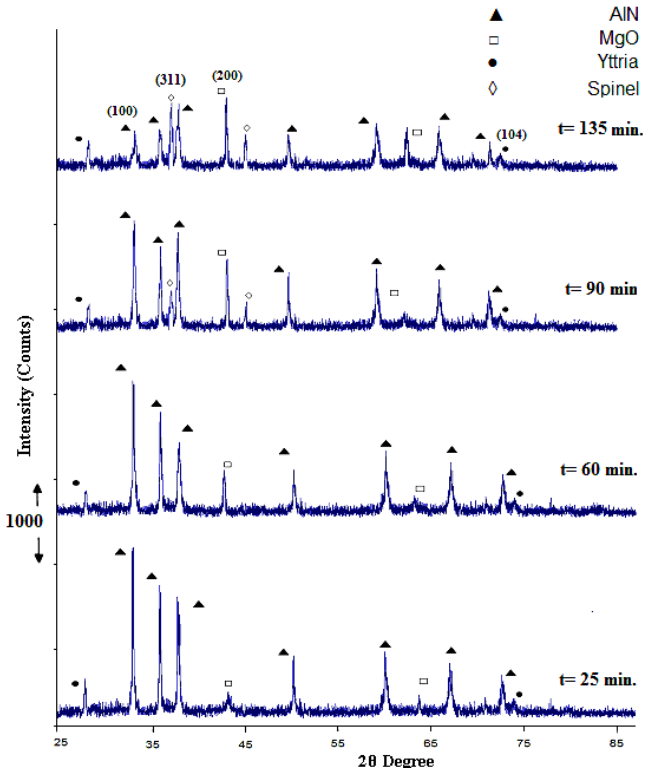

Figure 5- XRD patterns for infiltration at 950ºC with different holding times

In samples infiltrated at 650°C, as holding time increases, the quantity of MgO slightly increases and the amount of gamma phase increases as well. However, the quantities of aluminum nitride and aluminum phases are almost constant. Magnesium reduces due to evaporation and oxidation. At 800°C and 950°C, the effects of process time on the phase contents indicate that as holding time increases, the amount of AlN is reduced and the magnesium oxide content increases. In the samples processed at 950ºC, formation of spinel occurs at lower holding times (90 min) compared to 135 min for the case of 800ºC. Also, the rates of magnesia formation and aluminum nitride consumptions at 950°C are higher than those at 800ºC.

When magnesium volatizes and reacts with oxygen and nitrogen, magnesium oxide and magnesium nitride form. Magnesium vapor is an active gas because of its high vapor pressure. It reacts with oxygen and magnesium oxide forms according to:

$$Mg + \frac{1}{2}O_2 \rightarrow MgO \tag{3}$$

In samples infiltrated at temperatures higher than the oxidation temperature (>700ºC) of the AlN, alumina forms according to the following reaction:

$$4AlN(s) + 3O_2 \rightarrow 2Al_2O_3 + 2N_2 \tag{4}$$

And formation of more magnesium oxide is attributed to the reaction of the alumina film with magnesium:

$$Al_2O_3(s) + 3Mg(g) \rightarrow 2Al(l) + 3MgO(s) \tag{5}$$

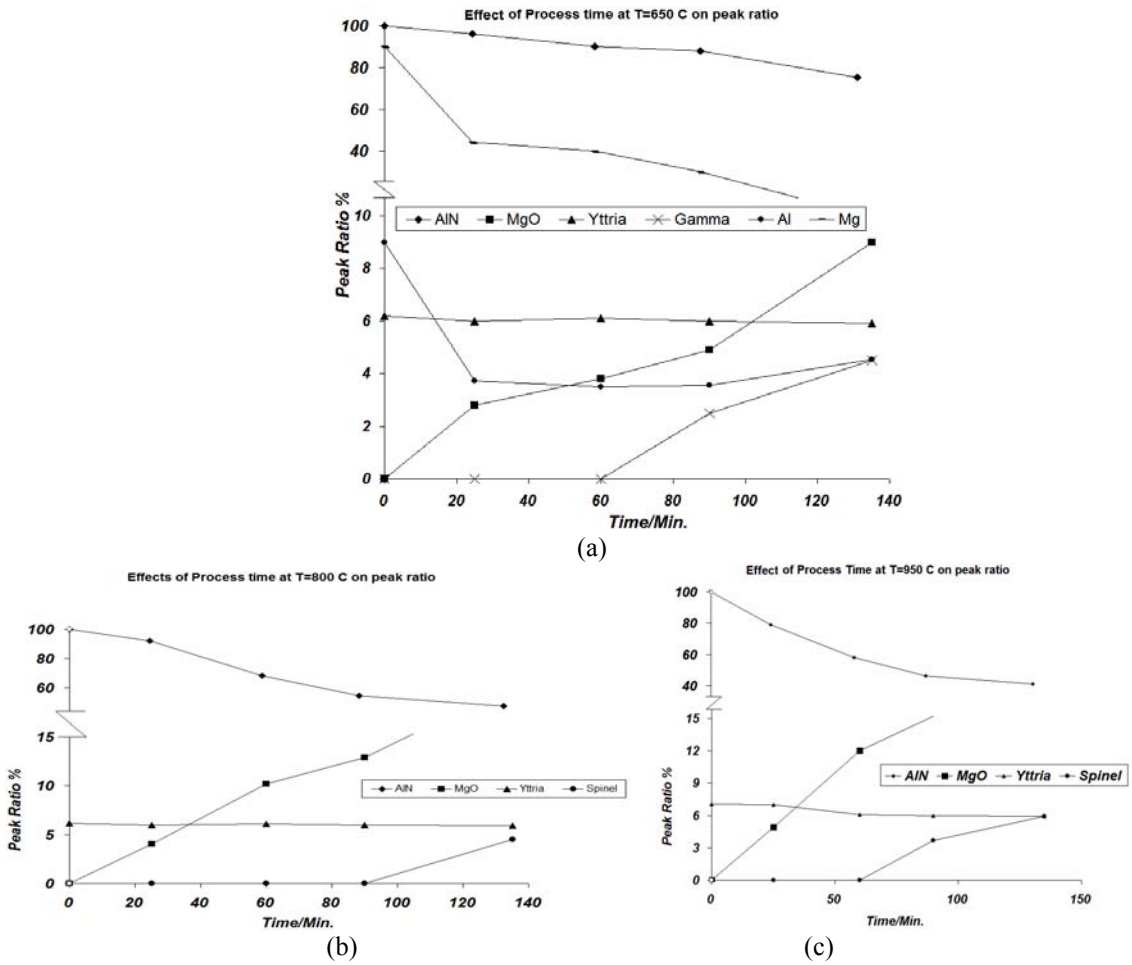

Figure 6- Effect of holding time on the phase contents of samples processed at: a) 650°C, b) 800°C, c) 950°C

Therefore, the rate of MgO formation is higher than observed for the samples processed at 650ºC. No metals were observed in the samples processed at 800ºC and 950°C. Suggesting that liquid aluminum reacted with nitrogen to form aluminum nitride according to:

$$2\,Al\,(l) + N_2\,(g) \rightarrow 2\,AlN\,(s) \tag{6}$$

Formation of the $MgAl_2O_4$ occurs only in the samples processed at 800°C with 135 min holding time and 950°C with 90 and 135 min holding time because of the reaction of alumina with magnesia as:

$$MgO(s) + Al_2O_3(s) \rightarrow MgAl_2O_4 \tag{7}$$

Kevorkijian [13], Hou [14], and Shtessel [15] reported formation of magnesium nitride particles which coated the surface of AlN particles and induced pressureless infiltration through greatly enhanced wetting. Therefore, the successful infiltration of magnesium into AlN performs is attributed to formation of a thin layer magnesium nitride (Mg_3N_2) which forms on the surface of the AlN phase. Then, a substitution reaction takes place between magnesium nitride and aluminum to form aluminum nitride according to:

$$Mg_3N_2 + 2Al \rightarrow 2AlN + 3Mg \tag{8}$$

The needed molten aluminum to react with magnesium nitride was supplied from the magnesium alloy and as a product of the reaction between magnesium and alumina (Equation 5). In samples processed at 650ºC, molten aluminum is supplied only from the magnesium alloy (AZ91E), while in samples at 800, 950ºC it is supplied from melting magnesium alloy and through reaction 5, because AlN oxidation, which provides alumina to allow Equation 5 to proceed, takes place at higher than 700ºC (Equation 4).

Physical and Thermal Properties

The average porosity and relative density of composites, determined using the Archimedes' principle (ASTM standard C20-97) was 11.6 vol. % and 2.45 g/cm^3. All samples processed at 650ºC holding temperature are conductors and those at 800ºC and 950ºC are insulators (Table2). The presence of metallic phases in the samples processed at 650ºC, of course, made them conductors.

Table 2- Electrical resistance measurements

Samples Processed at		Bulk Electrical Resistivity of Samples (Ω.cm)	Bulk Electrical Resistivity of Replicas (Ω.cm)
Temp. (ºC)	Time (min)		
650	25	Conductor	N/A
650	60	Conductor	N/A
650	90	Conductor	N/A
650	135	Conductor	N/A
800	25	6.73×10^9	1.19×10^{10}
800	60	5.73×10^{10}	9.98×10^9
800	90	1.44×10^{11}	2.65×10^{11}
800	135	2.27×10^{11}	3.98×10^{11}
950	25	1.42×10^{11}	9.8×10^9
950	60	1.85×10^{11}	1.85×10^{11}
950	90	2.04×10^{11}	3.45×10^{11}
950	135	2.10×10^{11}	6.58×10^{11}

Figure 7 shows the thermal diffusivity and heat capacity measured on composite products between 30°-295°C. In all samples, thermal diffusivity decreased with increasing temperatures, but at different rates depending on the porosity content and bulk density. The trend of heat flow for all holding times is similar and almost constant.

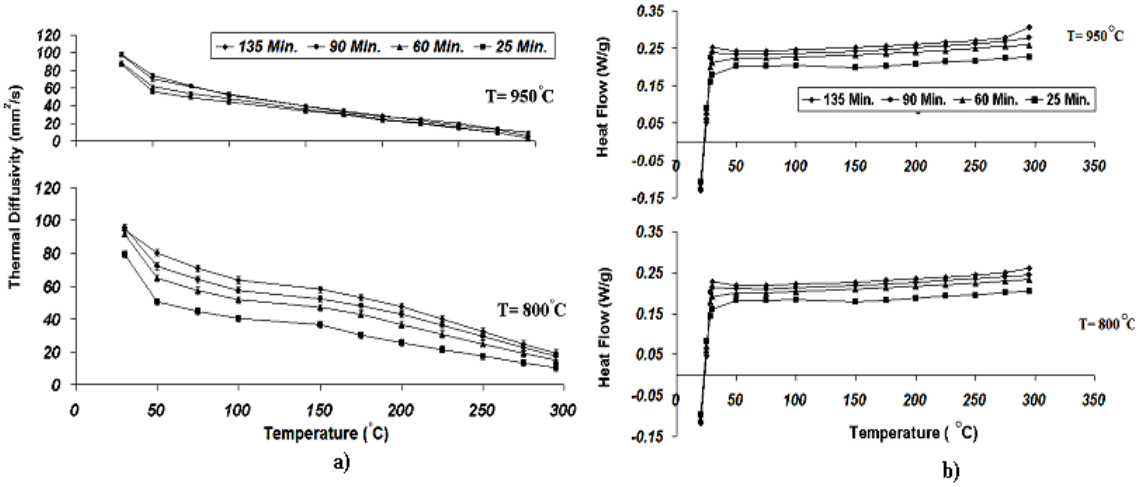

Figure 7- a) Thermal diffusivity and, b) Heat capacity of samples processed at 800°C and 950°C

Based on the specific heat capacity, thermal diffusivity, and density values, thermal conductivity has been plotted in Figure 8. For the 950ºC and 135 min. condition, the maximum thermal conductivity value of 95.88 W/m.K was achieved.

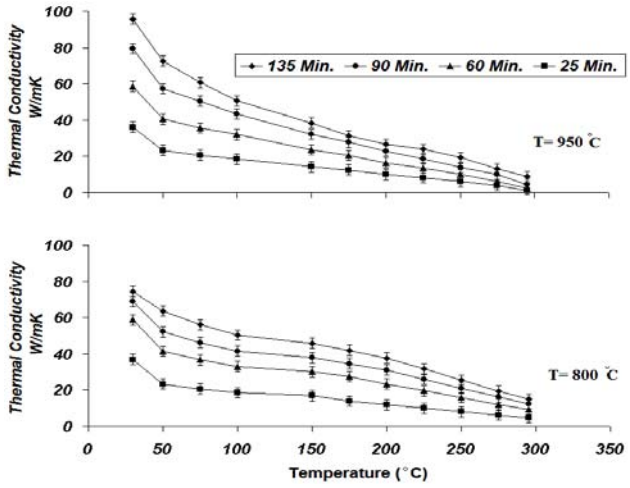

Figure 8- Thermal conductivity versus temperature calculated with constant heat capacity

In samples with high density, thermal diffusivity increased because heat transfer across pores is ordinarily slow and inefficient. Therefore, thermal conductivity is influenced by the residual porosity. The variation of thermal diffusivity and conductivity with porosity has been plotted in Figure 9.

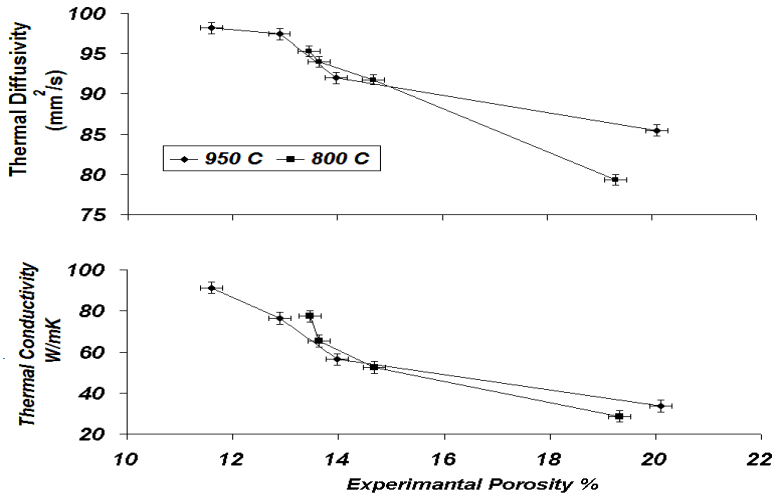

Figure 9- Effect of porosity on thermal conductivity and diffusivity for 800ºC and 950ºC processing

Conclusions

1. A simple and low cost procedure to fabricate AlN/MgO and AlN, MgO, MgAl2O4 composites with in-situ spontaneous infiltration at low temperature (<1000°C) was developed.

2. The proposed mechanism for complete infiltration is based on the formation of Mg_3N_2 phase, which completely or partially coats the AlN preform and enhances wetting.
3. The pressureless infiltration occurs at relatively low temperature (650-950ºC) in two directions, downward and upward simultaneously using proper compaction of the AlN preform.
4. The maximum thermal conductivity value, 95.88 W/m.K, was obtained for the sample processed at 950 ºC and 135 min.

NOMENCULATURE

C_p	Heat Capacity (J/gºC),
H	Heat Flow (W/g)
K	Thermal Conductivity (W/mK)
R	Electrical Resistivity (Ω.cm)
t	Holding Time (min)
T	Temperature (ºC)
D	Thermal Diffusivity (mm^2/S)
ρ	Density (g/cm^3)

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