METABK 55(4) 793-795 (2016)
UDC – UDK 666.31:621.775:661.55:620.17:620.18=111

GASS PRESURE SINTERED Si_3N_4 – $MgSiN_2$ COMPOSITES

Received – Prispjelo: 2015-11-06
Accepted – Prihvaćeno: 2016-03-30
Preliminary Note – Prethodno priopćenje

Si_3N_4 and $MgSiN_2$-based ceramic composites have excellent thermo-physical and mechanical properties, however with limited industrial applications. In this paper the preparation of Si_3N_4/$MgSiN_2$ composite by gas pressure sintering (GPS) is described and some of the mechanical properties like Vickers hardness and indentation fracture are characterised and compared with hot pressed (HP) samples. The 15,3 GPa hardness and 7,6 MPa·$m^{1/2}$ fracture toughness of GPS composites was slightly lower compared to HP samples (16,5 GPa, 8 MPa·$m^{1/2}$).

Key words: ceramic, powder, composites, nitridation, mechanical properties.

INTRODUCTION

Silicon nitride based ceramics are intensively studied for more than 40 years as engineering materials due to their excellent mechanical properties [1]. Polycrystalline Si_3N_4 ceramics have a high strength (800 - 1 200 MPa), fracture toughness (6 - 10 MPa×$m^{1/2}$) and good creep resistance. The hardness of β – Si_3N_4 is 14 - 16 GPa, while the hardness of a - Si_3N_4, is higher, 21 GPa [2]. Despite these good mechanical properties there is still a high interest to improve some properties of Si_3N_4 ceramics and especially decrease the price of ceramic products and promote the wider industrial application of this material [3].

Magnesium silicon nitride ($MgSiN_2$) is intensively studied in the recent years, as an alternative material for the substrates of the integrated circuitsowing to its good thermal conductivity and high electrical resistance [4]. $MgSiN_2$ has high hardness (20 GPa), reasonable strength (280 MPa), and fracture toughness (3 MPa×$m^{1/2}$), which makes it suitable for some engineering applications [5]. In this work Si_3N_4 – $MgSiN_2$ composites were prepared by two different sintering methods, by gas pressure sintering (GPS) and by hot pressing (HP) and their mechanical properties were evaluated. Although HP is more effective sintering method for the preparation of dense ceramic composites, the shape variety of products is limited. For that reason also GPS method was tested, which allows the sintering of ceramics with complicate shape and is more suitable for industrial applications.

EXPERIMENTAL METHOD

$MgSiN_2$ powder is not available on the market, for that reason it was prepared in lab from the mixture of Mg_2Si (99 %, Kojundo Chem. Lab., Japan), a - Si_3N_4 (grade SN-E10, Ube Industries Ltd., Japan) and Si (99,9 %, Kojundo Chem. Lab., Japan). The composition of starting powder mixture was calculated according to the following equation:

$$y \cdot Mg_2Si + (1 - 3 \cdot x - y)\ Si + x \cdot Si_3N_4 + (1 - 2 \cdot x)\ N_2 = MgSiN_2 \quad (1)$$

Where y = 0,5 and x = 0,06. This starting powder mixture is depicted as MSN – s1. The details of $MgSiN_2$ powder preparation, i.e. temperature and gas regime are described elsewhere [6]. The same a - Si_3N_4 powder (SN-E10, Ube) was used also for the matrix of composites, Yb_2O_3 and Lu_2O_3 (both from Treibacher AG, Austria) were used as sintering additives. The compositions of starting powders for the preparation of Si_3N_4 – $MgSiN_2$ composites are listed in Table 1. The number in the sample name shows the $MgSiN_2$ content, i.e. SMN – 20 sample is composed of 20 % $MgSiN_2$ and 80 % Si_3N_4.

It was shown that Yb_2O_3 and Lu_2O_3 as sintering additives improves the room and high-temperature properties of Si_3N_4 and $MgSiN_2$ ceramics [7-9]. Itatani et al. reported that the addition of 1 mol.% Yb_2O_3 sintering aid is sufficient for the densification of Si_3N_4 – $MgSiN_2$ composites by hot pressing at 1 600 °C [10].

Table 1 **Composition of starting powders for the preparation of Si_3N_4 – $MgSiN_2$ composites**

Sample	Si_3N_4 / wt.%	MSN-s1 / wt.%	Yb_2O_3 / wt.%	Lu_2O_3 / wt.%
SMN – 5	78,78	3,22	8,96	9,04
SMN – 10	75,62	6,1	9,1	9,19
SMN – 20	69,02	12,09	9,4	9,49
SMN – 30	62,07	18,41	9,72	9,81
SMN – 40	54,72	25,09	10,05	10,15
SMN – 50	46,94	32,15	10,4	10,51
SMN – 80	20,59	56,09	11,6	11,72

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The samples were nitrided at 1 390 °C (bellow the melting point of Si) for 4 hours under 0,107 MPa nitrogen atmosphere. After nitridation the samples were further densified either by hot-pressing or GPS. Samples were hot pressed at 1 600 °C for 1 hour under 30 MPa pressure in nitrogen atmosphere (0,1 MPa). The temperature and gas regime applied during GPS is listed in Table 2.

Table 2 **Temperature and gas regime applied during GPS of Si_3N_4 – $MgSiN_2$ composites**

Rate / °C/min	*T* / °C	Dwell / min	*P* (N_2) / MPa
30	800	0	0,2
15	1 500	0	0,8
10	1 600	120	3,0
15	1 300	0	2,0
25	25	END	0,1

The phase composition was investigated using powder X-ray diffraction (PAN analytical, Empyrean, Cu K_α radiation) in the range 2 Θ = 15° – 80°. The microstructure was observed by scanning electron microscopy (Zeiss EVO40 equipped with EDX analyser, Bruker AXS) on polished and plasma etched (Plasma System-Femto, DienerElectronicGmbH) cross sections of samples. Vickers hardness and fracture toughness were measured using Leco hardness tester (LV-100, Leco Co., USA) by indentation method with a load of 9,8 N and 98 N, respectively. The indentation fracture toughness was calculated according to Shetty equation [11]:

$$K_{IC} = 0{,}0889(H \cdot P/4l)^{0,5} \quad (2)$$

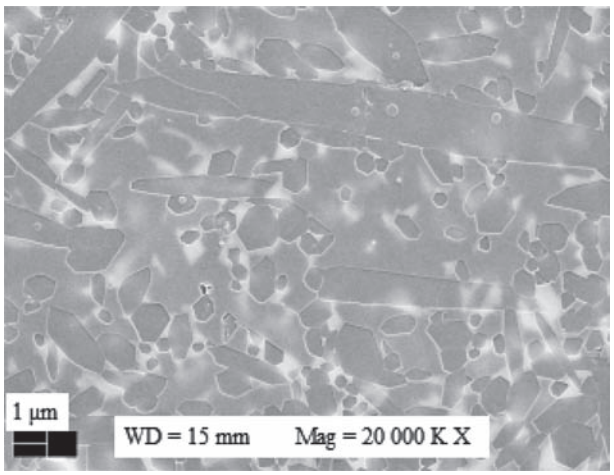
Where H is the hardness, P the applied load and l the crack length. It should be mentioned that the indentation method overestimates the values of K_{IC} compared to notch methods (V-notch, Chevron notch, etc.) [12].

RESULTS AND DISCUSSION

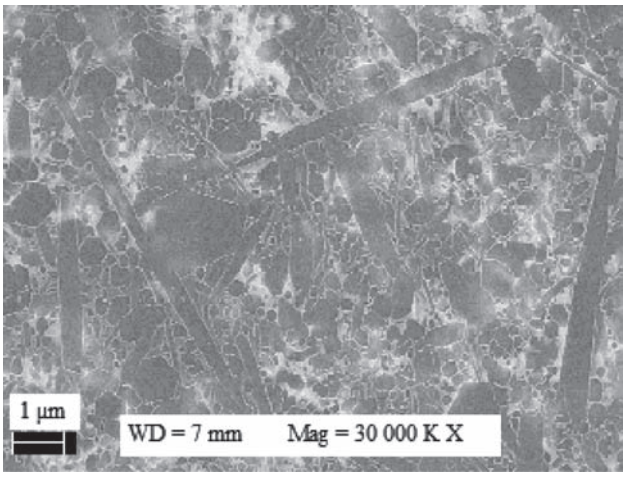
Microstructure

The density measurements and sample cross section analysis showed that the hot-pressed samples reached full density, while the GPS samples containing 5 and 10 % of $MgSiN_2$ had some residual porosity (3 – 7 %). These results indicate that except of the sintering additives also $MgSiN_2$ supported the densification of composites.

The microstructure of sample SMN – 40 densified by GPS method is shown in Figure 1 a. The etched elongated and hexagonal shaped particles are β – Si_3N_4, the unmatched grey particles are $MgSiN_2$ and the white amorphous phase is on the base of sintering additives (Yb_2O_3 and Lu_2O_3) and SiO_2 impurity (always present on the surface of Si_3N_4 powder). With increasing $MgSiN_2$ content also the size of elongated β – Si_3N_4 increases and the GPS composites with 80 % $MgSiN_2$ have the coarsest microstructure. During GPS relatively high pressure of nitrogen was applied (3 MPa) and it is known that the higher dissolved nitrogen content in the liquid phase during sintering supports the growth of large β – Si_3N_4 grains [13]. On the contrary, Si_3N_4 composites with 5 and 10 % $MgSiN_2$ have a fine microstructure with thin elongated whisker-like β – Si_3N_4. These elongated β – Si_3N_4 grains have a positive influence on the fracture resistance of composites.



a)



b)

Figure 1 Microstructure of a) gas-pressure sintered SMN – 40 composite and b) hot-pressed SMN – 40 composite (bar 1 µm).

Mechanical properties

Although the GPS conditions were optimised, some of the GPS samples contained residual porosity which has a (negative) influence on the mechanical properties of ceramic composites. Despite the residual porosity the measured Vickers hardness values showed that with increasing $MgSiN_2$ content (harder phase compared to β – Si_3N_4) the hardness of composites increases. The highest hardness 15,4 GPa was observed for GPS sample SMN – 80 with 80 % $MgSiN_2$. Contrary to hardness, the fracture toughness of composites decreases with in-

creasing $MgSiN_2$ content, which has a lower toughness (3,7 MPa×$m^{1/2}$) compared to β – Si_3N_4 (6 – 8 MPa×$m^{1/2}$). The highest indentation fracture toughness 7,3 ± 0,4 MPa×$m^{1/2}$ was obtained for the GPS sample SMN – 5.

The hot pressed samples were fully dens and the highest values of *HV* and K_{IC} were obtained for the hot-pressed SMN – 30 sample, 16,3 ± 0,3 GPa and 8,0 ± 0,2 MPa×$m^{1/2}$, respectively.

The comparison of obtained *HV* and K_{IC} values shows that the HP samples have better mechanical properties compared to GPS samples. However, to our best knowledge the reported results for GPS samples are the best obtained for Si_3N_4 – $MgSiN_2$ composites sintered with this method. The GPS method is more suitable for industrial application compared to hot-pressing, because it allows to sinter much larger number of samples during one sintering run and there are no serious limits to the shape of samples.

The microstructure of hot-pressed Si_3N_4 – $MgSiN_2$ samples is finer compared to GPS samples. The microstructure of hot-pressed SMN – 40 sample is shown in Figure 1 b and is composed of elongated β – Si_3N_4 grains and equiaxed a - Si_3N_4 and $MgSiN_2$ grains. The white phase is the amorphous grain boundary phase containing the sintering additives.

CONCLUSION

The densification conditions of Si_3N_4 – $MgSiN_2$ composites by gas-pressure sintering and hot-pressing were optimised. The HP samples were fully dense and despite the small residual porosity of GPS samples, both composites have a good mechanical properties (*HV* ~ 15 – 16 GPa, K_{IC} ~ 7 – 8 MPa×$m^{1/2}$). These properties allow their wider industrial application in engineering, aeronautics, metallurgy, etc.

Acknowledgement

This work was financially supported by the projects VEGA-02/0178/10 and MŠMT ČR-SP 2012/196.

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Note: The responsible translator for the English language is Miriam Gabčová, Slovak Republic