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Effect of Sintering Additive Composition on the Mechanical and Tribological Properties of Si_3N_4/SiC Ceramics

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Abstract: Two compositions of the Y_2O_3-Al_2O_3 (YA) and Y_2O_3-MgO (YM) systems were chosen to investigate the effect of sintering additive composition on the mechanical and tribological properties of gas pressure sintered Si_3N_4/SiC ceramics. The relative density, flexural strength, fracture toughness, hardness, coefficient of friction and wear rate were verified to depend substantially on the sintering additive composition. Compared with YM, the Si_3N_4/SiC ceramics with YA exhibit superior sinterability and show preferable mechanical and tribological properties, especially for the Si_3N_4/SiC ceramics with 20wt% SiC addition. These properties can be primarily attributed to the higher relative density and the grain size with smaller aspect ratio.

Key words: Si_3N_4/SiC ceramics; sintering additive; flexural strength; tribological properties

Silicon nitride-based ceramics are potential material for a variety of structural applications because of their superior mechanical properties including low thermal expansion, high hardness, good creep as well as favorable oxidation resistance, which allow them to be used in tribological applications such as valves, ball bearings, cutting tools, *etc*[1-2]. The mechanical properties of Si_3N_4-based ceramics have been modified by incorporating the second phase (like TiC, TiN, B_4C, SiC, *etc*) in the form of platelets, whiskers or particles, and a significant improvement has been achieved in flexural strength, fracture toughness and creep resistance[2-3]. Si_3N_4/SiC composites have been recently prepared by doping the Si_3N_4 powder with amorphous SiNC precursor[4] or using carbothermal reaction[5] in order to improve hardness, strength and resistance to creep, oxidation and corrosion of Si_3N_4 ceramics. On the other hand, Kasiarova, *et al*[6] reported that the decreased fracture toughness and degraded flexural strength of Si_3N_4/SiC composite compared with the Si_3N_4 monolith were obtained.

Furthermore, with the aim of improving the mechanical and tribological properties of developed ceramics, there has been significant research concentrating on the influence of sintering additives and microstructures on the wear resistance of Si_3N_4 based ceramics. Miyazaki, *et al*[7] reported that with Y_2O_3 and Al_2O_3 sintering additive, both hardness and fracture resistance did not show any direct relationship to the specific wear rate after being measured in the ball-on-disk test. But some authors reported that the wear resistance was improved owing to the decreased Si_3N_4 grain size despite the decreased fracture toughness[8-9]. For Si_3N_4/SiC composites, however, some authors reported that the pullout of SiC whiskers resulted in higher wear resistance compared with the monolithic Si_3N_4, while others observed that there was only slight difference between their wear performance[4,10]. Thus, a clear relationship between the tribological characteristics and the grain size and mechanical properties was not revealed. Hyuga, *et al*[11] showed that the wear properties of Si_3N_4 ceramics can be tailored by selecting the appropriate kinds of sintering additive. The wear mechanism was also affected by the factors such as temperature, atmospheric humidity, sliding speed and contact load[12-17].

In this study, Si_3N_4/SiC ceramics were prepared by gas pressure sintering (GPS), with raw materials of commercially available Si_3N_4 and SiC powders, two compositions of the YA and YM systems as sintering additives, and their mechanical and tribological properties were investigated.

1 Experimental procedures

1.1 Materials Preparation

Commercially available α-Si_3N_4 (0.5 μm, purity≥95wt%, UBE Co., Ltd., Tokyo, Japan), α-SiC (0.5 μm, with a purity of 99.4wt%, Weifang Kaihua Silicon Carbide Micro- owder

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Co., Ltd., Weifang, China), Y_2O_3 (5.0 μm; purity ≥ 99.99wt%; Yuelong Company, Shanghai, China), α-Al_2O_3 (99.9wt% purity, an average particle size of 0.6 μm, Wusong Chemical Fertilizer Factory, Shanghai, China), and MgO (50 nm, purity≥99.9wt%, Aladdin Chemistry Co. Ltd, Shanghai, China) were used. The added SiC content in the composite was varied from 0 to 60wt%. Mixture series were prepared from the starting material powders of Si_3N_4 and SiC, and YA (Y_2O_3-Al_2O_3) or YM (Y_2O_3-MgO) was used as sintering additives with the weight ratio of YA (3:1) or YM (3:1) in 15wt% of the starting materials. The mixtures were ball-milled in ethanol for 24 h. After vacuum drying and sieving through 100 mesh screen (average size 150 μm), 2.5 g of powder mixture was uniaxially pressed in a stainless steel die under the pressure of 10 MPa. Then the samples were cold-isostatically pressed at a pressure of 200 MPa. The sintering of the green bodies was conducted in a graphite resistance furnace with heating procedure of 10℃/min to 1100℃, then temperature increased to 1800℃ at 3℃/min and kept for 4 h under a positive high-purity nitrogen pressure of 0.6 MPa.

1.2 Characterization

The specimens were machined into rectangle bars with a dimension of 3.0 mm×4.0 mm×36.0 mm to measure the flexural strength *via* the three-point bending test (Instron 5566, INSTRON, Norwood, MA); the support distance of 30.0 mm and a cross-head speed of 0.5 mm/min were used. The bulk density was determined by the Archimedes method using distilled water as medium. Crystalline phases of the sintered specimens were determined by X-ray diffractometry (XRD; D/MAX-RBX, Rigaku, Osaka, Japan) with Cu Kα radiation. After bending test, the fracture surfaces were carefully cleaned, and microstructural formation was characterized by scanning electron microscope (SEM; JEOL JSM-6390, Tokyo, Japan). A unidirectional ball-on-disk tribometer(CETR, UMT-2, Multi-Specimen Test System) was used to evaluate the friction and wear characteristics of sintered specimens in ambient conditions. Si_3N_4 balls (hardness: 13 GPa, Step Precision ceramics Co., Ltd, Shanghai, China) of 9.65 mm diameter were used as counter-body materials. Both Si_3N_4 balls and sintered pellets were ultrasonically cleaned with acetone before wear testing. Si_3N_4 ball was fixed in the ball holder so as to make a track from the central axis and the tests were conducted at a fixed linear speed of 0.5 m/s for 40 min(total sliding distance of 1200 m). The sliding tests were carried out at a 5 N load. During the tests runs, frictional forces were recorded using an electronic sensor to generate the real time coefficient of friction (COF) data. In order to investigate the wear mechanism, a detailed microstructural characterization of the as-worn surfaces were conducted using SEM(JEOL JSM-6390, Tokyo, Japan). The wear rate was calculated according to the following relation:

$$WR=(M_1-M_2)/(\rho\times P\times S) \quad (1)$$

M_1 is the specimen mass before sliding test (g), M_2 is the specimen mass after sliding test (g), ρ is the relative density of specimen, P is the normal load (N), S is the sliding distance (m). And the aspect ratio of β-Si_3N_4 grains was analyzed using the software of Image Pro Plus 6.0.

2 Results and discussion

Figure 1 shows the XRD patterns of the sintered specimens with YA or YM sintering additives for various contents of SiC addition. β-Si_3N_4 and SiC were the major phase, with $Y_2Si_2O_7$ as minor phase, as indicated in Fig. 1(a) and (b). And the peak intensity of β-Si_3N_4 decreased with increased SiC contents, while the peak intensity of SiC increased with increasing SiC contents. Because it was indicated that with more SiC added, the suppression of mass transport and α→β-Si_3N_4 phase transformation became significantly obvious during the solution-precipitation process.

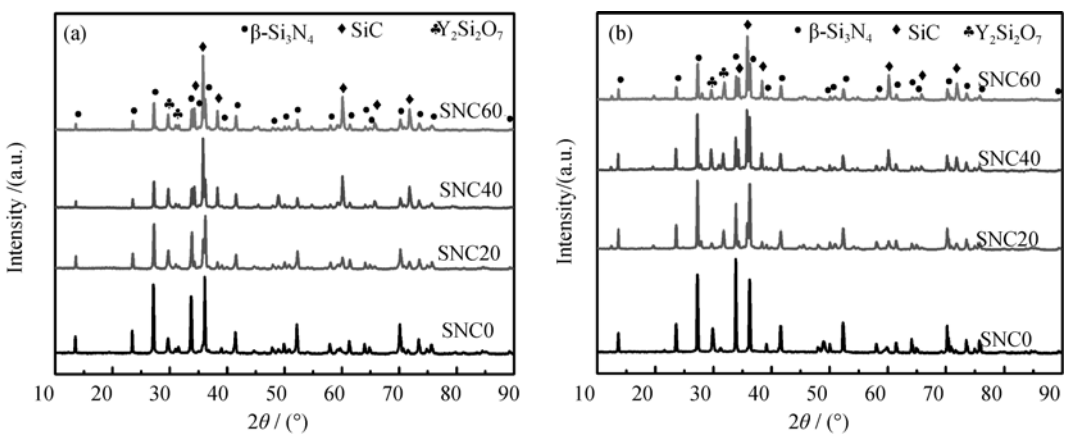

Fig. 1 XRD patterns of the sintered Si_3N_4/SiC ceramics with different sintering additives for various contents of SiC addition
(a) With YA sintering additive; (b) With YM sintering additive

In Fig. 2, with YA sintering additive, a relatively high densification (≥94% of theoretical density) was successfully achieved by GPS with 0−40wt% SiC addition at 1800℃ for 4 h. However, 40wt%−60wt% SiC added composite was not fully densified under the same sintering condition (~88wt% of theoretical density at 60wt% SiC addition). But in terms of YM sintering additive, the relative density of a 60wt% SiC added composite was only about 78%, even with 20wt% SiC addition, the highest obtained relative density was around 90%. Compared these two compositions of sintering additives, it was evident that the ceramics with YA showed better sinterability than that YM. However, in the case of using YA or YM with the same amount, Lee's results indicated that the higher relative density could be obtained with YM under certain sintering temperature and time owing to its lower melting point and lower viscosity[18]. The long holding period (4 h) at the maximum sintering temperature provided enough time for the complete α→β-Si_3N_4 phase transformation and the grain growth of Si_3N_4/SiC ceramics. The detected major phase of β-Si_3N_4 (Fig. 1) and larger diameter grains (Fig. 4) illustrate that very well.

Figure 3 and Fig. 4 show the fracture morphologies of

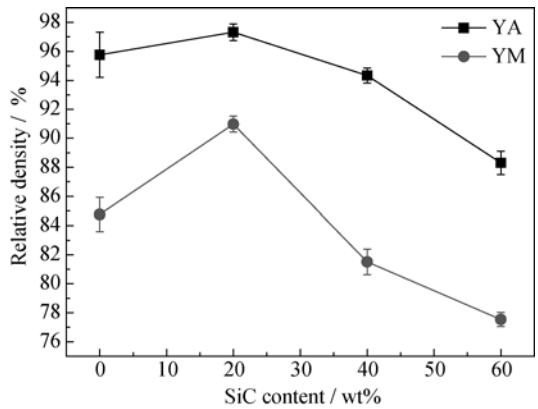

Fig. 2　Relative density of the sintered Si_3N_4/SiC ceramics with YA or YM sintering additive for various contents of SiC

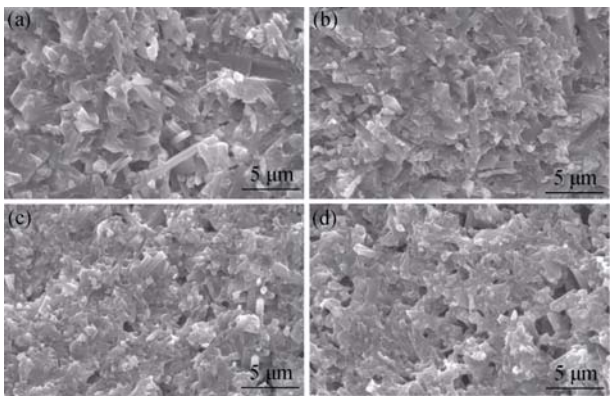

Fig. 3　SEM fracture morphologies of the sintered Si_3N_4/SiC ceramics with YA sintering additive for (a) without SiC, (b) 20wt% SiC, (c) 40wt% SiC and (d) 60wt% SiC addition

prepared Si_3N_4/SiC composite ceramics. With two compositions of YA and YM sintering additives, the interlocking morphology of Si_3N_4/SiC ceramics has been achieved and the diameter of grain was smaller for the achieved former materials. Both achieved highest relative density with 20wt% SiC addition. With higher content of SiC, the size of β-Si_3N_4 grains gradually decreased, which suggested that the growth of β-Si_3N_4 grains was restrained by the SiC during the solution-precipitation process. This can be attributed to grain-boundary pinning due to SiC dispersion, resulting in higher aspect ratio of β-Si_3N_4 grains. In addition, SiC was hard to be sintered, it can act as grog addition to maintain an open pore structure in the specimens leading to the decrease of relative density. Thus, with the content of 40wt% or 60wt% SiC, some pores appeared in the structure, as shown in Fig. 3(c,d) and Fig. 4(c, d).

The flexural strength, elastic modulus and hardness of the developed Si_3N_4/SiC composite ceramics with YA or YM sintering additive all firstly increased and then decreased as the SiC content increased. In Fig. 5 and Table 1, at each fixed content of SiC, the flexural strength, the elastic modulus and hardness with the YA surpassed that with YM. This could be accounted for the decreased relative density which was brought about by the large diameter grains with interlocking morphology. At the content of 20wt% SiC, Si_3N_4/SiC ceramics with either YA or YM both reached the highest flexural strength, elastic modulus and hardness. The fracture toughness also firstly increased and then decreased with further more SiC addition. But the fracture toughness with YM was superior to that with YA when the content of SiC addition varied from 0 to 40wt%. This can be attributed to the higher percentage of large grains in the matrix with YM sintering additive. Thus, the improved mechanical properties of Si_3N_4/SiC ceramics both have been prepared with YA and YM sintering additive at 1800℃ for 4 h, although the mechanical properties

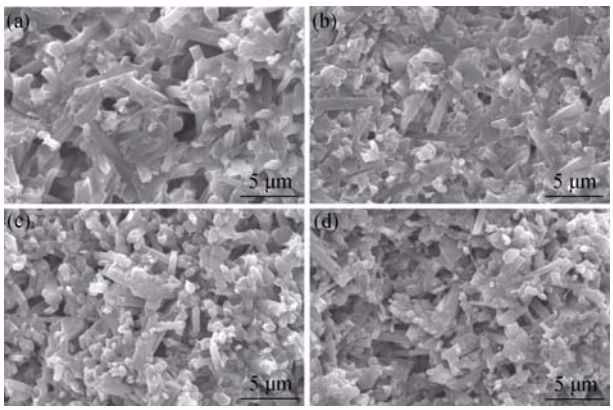

Fig. 4　SEM fracture morphologies of the sintered Si_3N_4/SiC ceramics with YM sintering additive for (a) without SiC, (b) 20wt% SiC, (c) 40wt% SiC and (d) 60wt% SiC addition

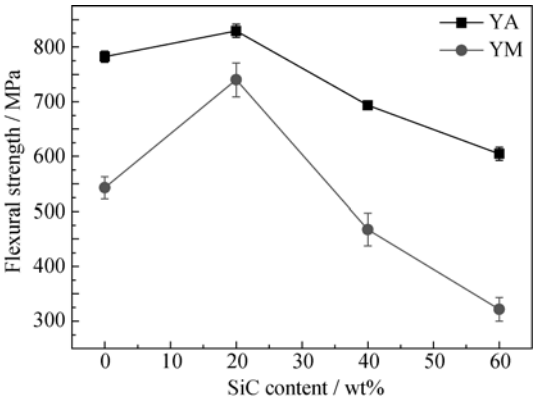

Fig. 5 Flexural strength of the sintered Si_3N_4/SiC ceramics with YA or YM sintering additive for various contents of SiC

showed an obvious difference. Moreover, it was reported that Si_3N_4/SiC ceramics with improved hardness and fracture toughness could be obtained with SiC addition up to 20wt% (Hardness: 18.1 GPa; Fracture toughness: 3.57 MPa·m½)[19].

As shown in Fig. 6(b,c,d), some wear debris adhered to the edges of track and the extent of typical plough zones decreased with more SiC added, compared with no SiC added, in Fig. 6(a). Some large holes can also be detected on the worn suface in Fig. 6(a), as the embedded higher magnification image indicated. However, the severe delamination can be observed on the worn surfaces in Fig. 7(a,c,d), while the worn surface of the sample with 20wt% SiC addition (Fig. 7(b)) was smooth and covered with oxide film, as can be seen in embedded higher magnification image.

When subjected to unlubricated sliding against Si_3N_4 balls, the sintered Si_3N_4/SiC composite ceramics with YA or YM sintering additive exhibited a steadily decreased value of coefficient of friction (COF) for the various contents of SiC addition (Fig. 8). This was attributed to the excellent corrosion resistance due to the SiC addition.

Meanwhile, the value of COF and the wear rate with YA was generally lower than that with YM. This can be explained by the higher relative density and the smaller grain size. With YA sintering additive, the relative density of the sintered Si_3N_4/SiC composite ceramics was 95.8%, 97.3%, 94.3%, 88.3% for 0, 20wt%, 40wt%, 60wt% SiC addition, while that was 84.8%, 91.0%, 81.5%, 77.5% with YM sintering additive (Fig. 2). The aspect ratio of grain size with YA sintering additive was smaller than that of with YM sintering additive, especially for 20wt% SiC with aspect ratios of 1.89 (YA) and 2.01 (YM), respectively, as indicated in Fig. 3 and Fig. 4. It was indicated that the wear resistance of Si_3N_4 and its based ceramics was apparently improved owing to the reduced grain size[19-21]. Thus, the

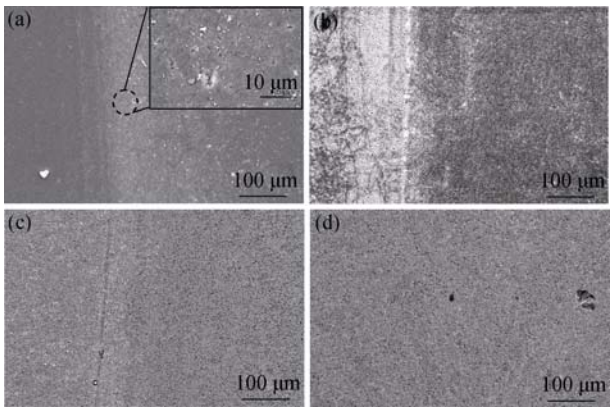

Fig. 6 SEM images of worn surface of the sintered Si_3N_4/SiC ceramics with YA sintering additive for (a) without SiC, (b) 20wt% SiC, (c) 40wt% SiC and (d) 60wt% SiC addition

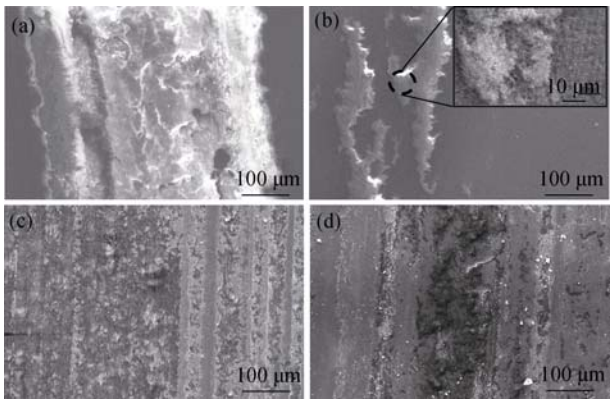

Fig. 7 SEM images of worn surface of the sintered Si_3N_4/SiC ceramics with YM sintering additive for (a) without SiC, (b) 20wt% SiC, (c) 40wt% SiC and(d) 60wt% SiC addition

Table 1 Elastic modulus, hardness and fracture toughness of the sintered Si_3N_4/SiC ceramics with YA or YM sintering additive for various contents of SiC

Samples	Elastic modulus/GPa	Hardness/GPa	Fracture toughness/(MPa·m$^{1/2}$)
YA	271	10.8±0.24	4.02±0.03
YA-20wt%SiC	311	14.6±0.10	4.12±0.01
YA-40wt%SiC	272	13.5±0.39	3.92±0.22
YA-60wt%SiC	251	11.8±0.35	3.93±0.02
YM	187	5.8±0.14	4.06±0.04
YM-20wt%SiC	242	10.3±0.39	4.93±0.13
YM-40wt%SiC	176	5.8±0.20	4.24±0.04
YM-60wt%SiC	142	3.6±0.15	2.92±0.12

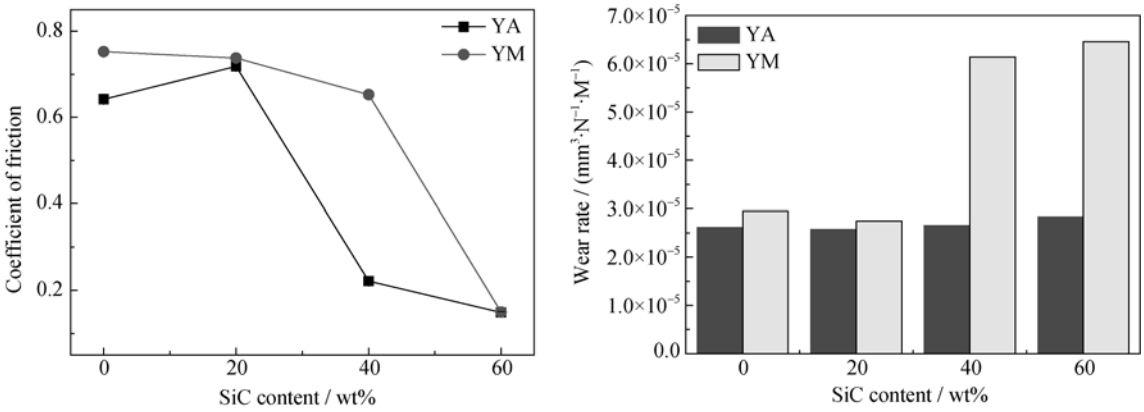

Fig. 8　Average coefficient of friction and wear rate of the sintered Si_3N_4/SiC ceramics with YA or YM sintering additive

sintered Si_3N_4/SiC ceramics with YA sintering additive showed the lower COF and higher wear resistance resulting from higher relative density and smaller grain size. The developed Si_3N_4/SiC ceramics with favorable mechanical and tribological properties can also be obtained with YA sintering additive for 20wt% SiC.

3　Conclusions

The effects of Y_2O_3-Al_2O_3(YA) and Y_2O_3-MgO(YM) sintering additives on the mechanical and tribological properties of gas pressure sintered Si_3N_4/SiC ceramics are investigated. The Si_3N_4/SiC ceramics with YA show favorable mechanical and tribological properties compared with YM, primary because the former contains a higher relative density and grain size with smaller aspect ratio. This is particularly pronounced in the Si_3N_4/SiC ceramics with YA for 20wt% SiC addition obtaining optimized mechanical and tribological properties.

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烧结助剂种类对 Si_3N_4/SiC 陶瓷力学与摩擦性能的影响

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摘 要: 分别以 Y_2O_3-Al_2O_3(YA)和 Y_2O_3-MgO(YM)为烧结助剂, 采用气压烧结工艺制备了 Si_3N_4/SiC 陶瓷, 研究了两种不同的烧结助剂对陶瓷的力学和摩擦性能的影响。研究结果表明: 添加不同种类的烧结助剂对制备陶瓷的相对密度、抗弯强度、断裂韧性、硬度、摩擦系数和磨损率影响很大; 与添加烧结助剂 YM 相比较, 添加烧结助剂 YA 的 Si_3N_4/SiC 陶瓷在烧结过程中表现出了更好的烧结性能, 得到的陶瓷样品最终显示了更好的力学和摩擦性能, 尤其是 SiC 添加量为 20wt%的 Si_3N_4/SiC 陶瓷。这主要归因于烧结助剂 YA 的添加使 Si_3N_4/SiC 陶瓷呈现出了更高的相对密度, 获得的晶粒长径比更小。

关 键 词: Si_3N_4/SiC 陶瓷; 烧结助剂; 抗弯强度; 摩擦性能

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