Journal of Alloys and Compounds 766 (2018) 678–685

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of surface nano-modification on the antioxidation properties of Si_3N_4 ceramics

Shuwei Cao [a, b, *], Yue Zhang [a, **], Dahai Zhang [b], Jingyi Zhang [b], Jun Zhou [b], Juan Zhang [b], Xiaoming Liu [b], Jian Zhang [b]

[a] Key Laboratory of Aerospace Advanced Materials and Performance, School of Materials Science and Engineering, Beihang University, Beijing, 100191, China
[b] National Key Laboratory of Advanced Functional Composite Materials, Aerospace Research Institute of Materials and Processing Technology, Beijing, 100076, China

ARTICLE INFO

Article history:
Received 10 April 2018
Received in revised form
26 June 2018
Accepted 29 June 2018
Available online 30 June 2018

Keywords:
Si_3N_4
Nano-SiO_2
Surface modification
Antioxidation
Flexural strength

ABSTRACT

The application of Si_3N_4 ceramics is effectively limited due to the catastrophic failure which is caused by the oxidation weight gain. Nano-modification on the surface of Si_3N_4 micropowders is prepared to reduce the oxidation weight gain of Si_3N_4 ceramics. After modification, the Si_3N_4 particles are encapsulated completely by spherical nano-SiO_2, which can obviously reduce the oxidation weight gain of the Si_3N_4 ceramics for the good sealing effect of dense SiO_2 coatings. The finally oxidation weight gain rate of the Si_3N_4 ceramics reduces about 54.3% at 1580 °C. The nano-SiO_2 coatings can also increase the surface area of Si_3N_4 particles, which can improve the sintering extent of the Si_3N_4 ceramics through accelerating the gradual strengthening of bonding necks between Si_3N_4 particles. The flexural strength of the Si_3N_4 ceramics without sintering additives is 78 MPa. The dielectric constant is 3.47 while the dielectric loss is 0.001, which satisfies the dielectric conditions of radomes.

1. Introduction

As a kind of high-temperature resistance structural ceramic, Si_3N_4 has been wildly applied in high-temperature gas filter, high speed cutting tools, bearing and sealing, gas turbine engines and different components in the aircraft's auxiliary power units due to its high-temperature strength, superior oxidation resistance, high fracture toughness, thermal shock resistance and excellent dielectric properties [1–8]. Recently, Si_3N_4 attracts much attention as the radome and antenna windows materials [9,10]. The antenna radome, which plays an important part role in the protection for the vehicles from severe high temperatures plus oxidizing conditions, requires materials possess high structural reliability and excellent dielectric properties [11]. However, the application of Si_3N_4 ceramics in radome materials is largely limited due to the catastrophic failure which is caused by the volume expansion for its oxidation weight gain [12–16]. The oxidation weight gain and volume change are mainly caused by the SiO_2 from oxidized Si_3N_4 and the volume expansion of the secondary phases (sintering additive, such as Y_2O_3, Al_2O_3) at high oxidation temperature, which reduce the strength and the reliability of radome [17]. To solve this problem, preventing oxidation and incorporating of low thermal expansion coefficient second phase in Si_3N_4 ceramics is desirable.

SiO_2 has excellent oxidation resistance, high-chemical stability, high-softening temperature, extremely low coefficient of thermal expansion and rather low-dielectrics, which make it an attractive structural/functional material [18]. SiO_2 is one of the excellent candidate materials as the low thermal expansion coefficient second phase in Si_3N_4 ceramics to prevent the oxidation of Si_3N_4 ceramics. Many recent studies have introduced amorphous SiO_2 to increase the reliability of Si_3N_4 ceramics by pre-oxidation or infiltration process. Lee and co-workers investigated the effect of SiO_2 content in the Si_3N_4 ceramics on the micro-structure, mechanical and dielectric properties. The results showed the flexural strength and the dielectric constant decreased with increasing SiO_2 content [10]. Qadirb et al. studied the influence of the oxidization of Si_3N_4 starting powder on the microstructural and mechanical properties of the Si_3N_4 ceramics. The Si_3N_4 powders were oxidized for 10 and 20 h respectively at 1000 °C in air to form amorphous SiO_2 layer before hot isostatic pressed. Decreasing flexural strength was

* Corresponding author. Key Laboratory of Aerospace Advanced Materials and Performance, School of Materials Science and Engineering, Beihang University, Beijing, 100191, China.
** Corresponding author.
E-mail address: caoshuwei@126.com (S. Cao).

https://doi.org/10.1016/j.jallcom.2018.06.363
0925-8388/

observed with the oxidation time [3]. Zhang et al. fabricated a porous Si_3N_4 ceramic using the pre-oxidation process to improve the mechanical and dielectric properties of Si_3N_4 ceramics. The flexural strength of the pre-oxidized specimens decreased to 14.2 MPa at 1300 °C, but finally increased to 25.6 MPa at 1400 °C [19]. Li et al. fabricated a porous Si_3N_4–SiO_2 composite ceramic via a novel process combining oxidation bonding with sol–gel infiltration sintering. The crystallization of oxidation-derived SiO_2 was avoided, the density, hardness, flexural strength and fracture toughness of the porous Si_3N_4–SiO_2 composite ceramic all increased with the increase of SiO_2 [18]. These attempts result in the decreasing flexural strength of Si_3N_4 ceramics, which reduce the reliability of Si_3N_4 ceramics. Sol–gel infiltration method has been proved to be effective to increase mechanical properties and avoid the oxidation of Si_3N_4 ceramics. But the distribution of amorphous SiO_2 in Si_3N_4 ceramics is inhomogeneous due to the complicated preparation process. The inhomogeneous SiO_2 could result in the appearance of coating crack for the shrinkage of the amorphous SiO_2 at high temperature, which can become into the weakness of stress and reduce the structure reliability of Si_3N_4 ceramics. In addition, the complicated preparation process brings the high cost and long cycle, which limits the engineering applications of the Si_3N_4 ceramics.

Herein, this work develops a novel route, to make homogeneous nano-modification on the surface of Si_3N_4 micro particles using nano-SiO_2, which can prevent oxygen from reacting with Si_3N_4 at high temperature. As known, the sintering additives, such as Y_2O_3 or Al_2O_3, are detrimental to the dielectric properties of Si_3N_4 ceramics. So in order to study the effect of the surface nano-modification, there is no other sintering additives except SiO_2 particles in the as-fabricated Si_3N_4 ceramic of this paper. The effect of the surface nano-modification on the antioxidation properties, the mechanical properties and the dielectric properties of Si_3N_4 ceramics are also studied in detail.

2. Experimental procedure

2.1. Sample preparation

Silica gel (15 wt. % SiO_2, 20 nm) and Si_3N_4 powder (300 nm, α-Si_3N_4≥95 wt%) are used as the raw materials (Fig. 1). Firstly, the Si_3N_4 powders are heat-treated at 600 °C in N_2 atmosphere for 1 h to remove the surface organic group. Secondly, the Si_3N_4 powders are put into deionized water to form Si_3N_4 slurry under constant magnetic stirring with a concentration of 8 wt%. When the Si_3N_4 slurry is heated to 60 °C, silica gel are added into the slurry in batches with a proportion of 2 wt% (SiO_2/Si_3N_4) for 4 h (S-1) to make nano-modification on the surface of Si_3N_4 micro particles. Then the slurry continues to be heated at 60 °C for 2 h. After constant magnetic stirring for 8 h, the slurry is sprayed drying and passes through a 120-mesh sieve. The raw Si_3N_4 powders (S-0) are treated in the same way except for the addition of silica gel to compare the modification effect of the nano-SiO_2. The green Si_3N_4 ceramics are fabricated by cold isostatic pressing (CIP) under a pressure of 200 MPa for 5min. In order to study the sintering behavior, the green Si_3N_4 ceramics are separately embedded in powder beds and sintered at 1000, 1200, 1400, 1550 and 1700 °C respectively in N_2 for 2 h with a heating and cooling rate of 5 °C/min. The as-fabricated Si_3N_4 ceramics are cut with a diamond saw, ground with a diamond whetstone, and polished with a diamond slurry to rectangular bars with dimensions of 3 × 4 × 36 mm for evaluations of mechanical properties. The influence of different nano-SiO_2 content on the oxidation resistance of Si_3N_4 ceramics is also studied (S-2, S-3). The Si_3N_4 ceramics with different nano-SiO_2 content are heated at 800, 1000, 1200, 1400 °C for 1 h in air to investigate the law of the oxidation weight gain rate.

2.2. Characterization

The microstructure of the fabricated materials is characterized by scanning electron microscopy (SEM, Quanta 650, FEI, America). The content of SiO_2 is tested by nitrogen oxygen determinator (TC600, leco, America). The phase compositions of the fabricated Si_3N_4 ceramics are characterized by X-ray diffraction (XRD, D8 Advance, Germany) with CuKα radiation. Voltage on Cuanode −40 kV, current intensity −40 mA, range of measurement angle 10–80°, speed of goniometer −1°/min. The oxidation behavior is evaluated by the simultaneous thermal analyzer (TGA-DSC, STA 449 F3 Jupiter, NETZSCH, Germany) from room temperature to 1580 °C at a heating rate of 10 °C/min in flowing air. The mechanical strength of the specimens is tested by an electronic universal testing machine (MTS, CMT5105). The size of flexural test pieces is 3 × 4 × 36 mm and flexural strength is evaluated by a three-point flexural test. The size of compression test pieces is 3 × 4 × 4 mm. Five specimens are tested for each condition to obtain the average strength. The dielectric constant and loss of the Si_3N_4 ceramics is tested by a resonantcavity method at 15.2 GHz [11]. Four specimens are tested to obtain the average dielectric constant and loss.

3. Results and discussion

3.1. The surface structure and sintering properties of the Si_3N_4

Fig. 2 shows the surface structure of the Si_3N_4 particles before and after surface nano-modification with different SiO_2 content (as is shown in Table 1). The surface of the raw Si_3N_4 particles is very smooth (Figs. 2 S-0). After surface nano-modification (Fig. 2 S-1), the surface of Si_3N_4 particles became roughly. The spherical nano-SiO_2 particles which are with the average diameter of 20 nm are

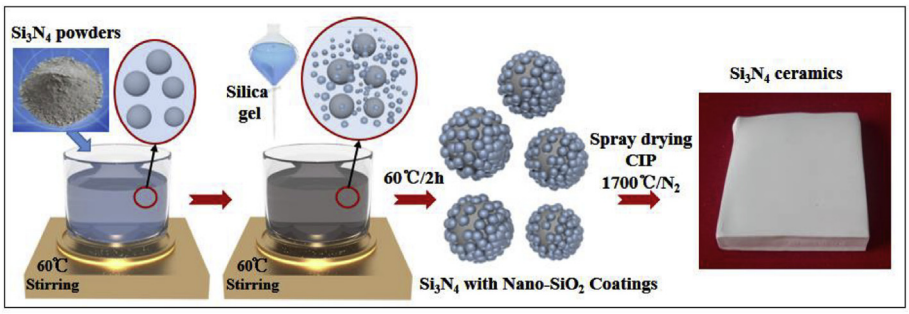

Fig. 1. Schematic of the surface nano-modification on the Si_3N_4 particles.