Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Dielectric properties of silicon nitride ceramics produced by free sintering

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ARTICLE INFO

Keywords:
Silicon nitride
Dielectric losses
Sintering

ABSTRACT

The silicon nitride ceramics with a beneficial combination of low dielectric losses and improved physical properties was fabricated by cold isostatic pressing and pressureless sintering. The fine grain microstructure, three-phase composition based on the β-SiAlON, the small amount of the glass phase and relatively small porosity promote a unique combination of a low thermal conductivity 14.51 W m^{-1} K^{-1} and low dielectric loss $1.4{\cdot}10^{-3}$. A novel method is proposed to overcome the main drawbacks of the commercial and high-cost technologies.

1. Introduction

The high performance silicon nitride ceramics has a great potential for aircraft and aerospace industry applications. An attractive combination of high strength, high oxidation resistance and low dielectric losses makes the silicon nitride ceramics interesting for a wide range of technical, industry and structural applications, such as gas turbine engines, next-generation power devices, turbocharger rotors, microwave devices and diesel engine components [1]. However, these properties typically have opposing characteristics, e.g., silicon nitride may be strong or exhibit low dielectric losses, but they are rarely both. The low dielectric losses of Si_3N_4 also make it a promising alternative candidate for the aviation and aerospace industry, namely, rocket production, antenna window and high speed missile radomes, the electrical insulators for a fusion powers reactor, such composite elements as aircraft missile, both front edges, missile warheads (nose cone) and the nozzle sleeve rocket engines, radio-windows, etc.

Common sintering additives are mixtures of such metal oxides as aluminum oxide, yttrium oxide and magnesium oxide. The most promising processing methods, which allow us the fabrication of advanced silicon nitride ceramics with improved mechanical properties, involve cold isostatic pressing (CIP) and pressureless sintering. It is well known, that the porosity in silicon nitride can be easily removed by such commercial methods as hot isostatic pressing (HIP) and spark plasma sintering (SPS). HIPed silicon nitride has substantially higher strength and ultimate tensile strengths with high levels of damage tolerance. To overcome the economic limitations of HIP and SPS, a process of cold isostatic pressing with a free low temperature and fast sintering was developed for application in the rocket industry. Due to the possibility of obtaining of complex shape and large size products the investigated method can be used as an economically and functionally superior alternative to other types of commercial methods. The proposed method can greatly reduce the cycle time to 60 min. As a result, this process can be applied for mass production.

At the same time, the dielectric constant and the dielectric loss tangent are the key factors for radioparency of ceramics. Porous Si_3N_4 ceramics have been developed to decrease the dielectric constant. In order to maintain high strength with low dielectric losses, it is desired to obtain fine grain microstructure and uniformly distributed small pores. It is one of the primary concerns in the processing of Si_3N_4 ceramics.

Thus, the main aims of the presented work are to report dielectric and physical properties of the pressureless sintered silicon nitride ceramics and to compare the mechanical and dielectric properties of silicon nitrides produced by different methods.

2. Material and methods

The initial Si_3N_4 powder was α-rich Si_3N_4 (Stark, Grade M11) with particle size of 600 nm with a high purity and high specific surface area. Y_2O_3 (Stark, Grade, 2 μm) and Al_2O_3 (A16 SG, 600 nm) sintering additives were used as starting materials. The mixture of powders was milled in the vibratory disc mill Retsch RS-200 for 20 min and, than, cold isostatically pressed at 200 MPa. Samples were heated using a constant heat rate of 25 °C min and sintered at 1650 °C, in a Nabertherm VHT 8 22-GR furnace under 0.1 MPa nitrogen pressure and using a silicon nitride powder bed. Other material and processing details were reported in previous work [2–4].

The dielectric loss tangent and permittivity were carried out using ET-1 device with OBR-1 and MDR-1 resonators in the temperature

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http://dx.doi.org/10.1016/j.ceramint.2017.03.161
Received 30 January 2017; Received in revised form 22 March 2017; Accepted 25 March 2017

range from 20 to 400 °C at 9 GHz.

Experimental samples were cut with a band saw from a sintered billet. One specimen from the batch was examined in a transmission electron microscope (JEOL-2100) at 200 kV. Foils for TEM were prepared from slices hand ground and finally ion-polished until perforation. Structural characterization was performed using scanning electron microscope and Quanta 600 FEG (FEI Company, Hillsboro, OR).

3. Theory

The molar heat capacity of produced ceramics was calculated by the Debye theory. The Debye temperature θ_D was calculated according to the following equation [5]:

$$\theta_D = \frac{h}{k_B}\cdot\left(\frac{9N}{4\pi V}\right)^{1/3}\cdot\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)^{-1/3} \quad (1)$$

where h is the Plank's constant, k_B is the Boltzmann's constant, N/V is the atomic concentration, $8.6\cdot10^{28}$ atoms/m^3, v_l is the longitudinal sound velocity, v_t is the transverse sound velocity. v_l and v_t were calculated as follows:

$$v_l = \sqrt{\frac{E(1-\nu)}{\rho(1-2\nu)(1+\nu)}} \quad (2)$$

$$v_t = \sqrt{\frac{G}{\rho}} \quad (3)$$

where G is the shear modulus, E is the Young's modulus, ρ is the material density and ν is the Poisson's ratio.

The elastic properties of the investigated material were measured by the resonance method and described in our previous work [2].

The molar isochoric heat capacity was calculated as follows [6]:

$$C_V = 3R\left[4D(x) - \frac{3x}{e^x - 1}\right] \quad (4)$$

where R is the molar gas constant, x is θ_D /T ratio (T is the temperature), and D(x) is the Debye function:

$$D(x) = \frac{3}{x^3}\int_0^x \frac{\xi^3}{e^\xi - 1}d\xi \quad (5)$$

This function was approximated by the sixth-degree polynomial by the least squares method.

The isochoric c_p heat capacity was described via the well-known relationship [7]:

$$c_p = c_v + V_m\cdot T\cdot\alpha_p^2/K_T \quad (6)$$

where V_m is the molar volume, c_v is the molar heat capacity, α_p is the coefficient of thermal expansion, $K_T=1/B_T$ is the isothermal compressibility coefficient.

The coefficient of thermal expansion was measured by Netzsch DIL 402C/4/G in temperature range of 20–900 °C.

The thermal diffusivity was measured by a laser flash method using a thermal constant analyzer LFA 457 Microflash Netzsch at room and elevated temperature from 20 to 500 °C. The thermal conductivity of the material can be estimated as:

$$k = \rho\cdot c_p\cdot\alpha \quad (7)$$

where k is the thermal conductivity, W/m K, ρ is the density kg/m^3, c_p-specific heat, J/kg K.

4. Results

Fully dense SiAlON was obtained by cold isostatic pressing and free sintering. Fig. 1 shows a microstructure of a polished specimen. The microstructure generally consisted of large and small equiaxed grains with a grain size distribution from 300 to 800 nm. The dielectric constant of the fabricated ceramics was 7.0 and the dielectric loss tangent was $1.4\cdot10^{-3}$ at room temperature. The dielectric loss tangent and the dielectric constant are plotted in Fig. 2 as functions of the temperature. The complex permittivity and dissipation factor of the specimens increase with an increase in the temperature. In particular, the dielectric loss tangent increases with an increase in the temperature from 20 °C to 350 °C. The highest dielectric loss tangent was observed at 400 °C. Further increase in the testing temperature up to 500 °C is accompanied with an increase in the dielectric loss tangent. Some dielectric and mechanical properties of silicon nitride ceramics produced by different methods are presented in Table 1. Table 1 shows that the investigated ceramics had a high density and low surface porosity (0.1%) [2].

It can be noted that the present ceramics has moderately low thermal conductivity 14.51 W m^{-1} K^{-1} and thermal diffusivity 5.92 m^2 s^{-1} (Table 2).

The Debye temperature of the present material was 804 K (Table 3) according to the Eq. (1). Fig. 3 shows the curve of the heat capacity calculated for obtained ceramics according to the Debye theory.

5. Discussion

XRD of produced ceramics showed that the microstructure of this material consists of two main phases: the α silicon nitride and β-SiAlON. By means of diffusion the fabricated ceramics featured such substitutional solid solutions as β-sialon Si_5AlON_7 as well as a small amount of $Y_2SiAlON_5$ (B-phase) [8]. The XRD analyses revealed β-Si_5AlON_7 (x=1) as a major phase. It was reported that the SiAlON with x < 1,5 are preferred as compared with the HIPed silicon nitride due to the lower dielectric losses [9]. The negative effect of MgO on the structure and physical properties in Si_3N_4 ceramics was identified in our previous work [10,11]. It was associated with the recrystallization and high sintering temperature. The higher sintering temperature of silicon nitride with Al_2O_3-MgO is caused by the higher melting point of MgO (2852 °C) compared with the melting point of Y_2O_3 (2425 °C). Also the dielectric loss tangent and dielectric permittivity of the MgO-Al_2O_3-SiO_2 alkali-free glass systems increases strongly with the increase in the concentration of MgO in the microwave range [9]. Thus, such additives as Al_2O_3- Y_2O_3 eventually lead to the optimal complex of dielectric and mechanical properties of produced ceramics. Silicon nitride ceramics are frequently used as high-temperature dielectrics and therefore the electrophysical properties are crucial for such materials. Ohno et al. showed that the dielectric loss tangent of the MgO and Al_2O_3-Y_2O_3 doped silicon nitride was $2\cdot10^{-3}$–$4\cdot10^{-3}$ at room temperature at 9.1 GHz and increased significantly to $10\cdot10^{-3}$–$15\cdot10^{-3}$ with an increase in the temperature up to 800 °C [12]. It's obvious that the glass phase had a higher dielectric loss tangent compared with the HPSN (hot pressed silicon nitride), because silica and such other additives as Ca^{2+}, Al^{3+}, Fe^{2+}, Na^+ and Cl^- were generally used for the glass phase formation [13–15].

Dielectrical properties of ceramics essentially depend on the developed microstructure. Fig. 1 shows the microstructures of the sintered ceramics. The figure shows the typical structure of SiAlON (Fig. 1). This structure is mostly homogeneous. Si_3N_4 particles with an essentially equiaxed hexagonal shape strongly dominate the material (Fig. 1). A low value of the dielectric loss tangent can be explained by the fine-grained microstructure consisting of fine equiaxed grains with the average size ranged from 0.3 to 0.8 μm as can be seen clearly from the SEM studies (Fig. 1b). These results have a good correlation with a similar TEM microstructure results (Fig. 1a). The microstructure of the ceramics has been described in detail in previous works [8]. Park et al. showed that increase in the grain size led to increase in the dielectric properties of the magnesium, yttrium and aluminum oxide doped hot pressed silicon nitride ceramics and found that an increase in the grain size from 0.5 to 3.5 μm led to increasing the tan δ from $1\cdot10^{-3}$ to $6\cdot10^{-3}$