Microstructural Evolution and Pressure-Assisted Master Sintering Surface of Silicon Nitride

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The pressure-assisted master sintering surface (PMSS) of silicon nitride has been constructed, in which the sintered density during hot pressing can be predicted as a function of the integral of a temperature function over time at a given pressure, irrespective of the heating path. High-purity α -Si₃N₄ powder with the additives of 6.25% Y₂O₃ and 1% Al₂O₃ was used for this research. Densifications of silicon nitride were continuously recorded during heating at two different ramping rates of 0.083°C/s and 0.167°C/s up to 1800°C at fixed pressures from 7 to 34 MPa. The activation energy was estimated as 698 kJ/mol. During the hot pressing, the microstructural evolution of α -Si₃N₄ to β -phase known as a solid/liquid/solid mechanism was also observed. Using the PMSS of silicon nitride, the final density can be predicted to about 1% accuracy for a fixed pressure and an arbitrary temperature-time path. [doi:10.2320/matertrans.MRP2008026]

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1. Introduction

Silicon nitride, being a covalently bonded ceramics of low self-diffusion coefficients, can be densified by using high sintering temperature and/or high pressures to promote diffusion or activate deformation processes. Thereby, in most cases, small amounts of oxides are used as sintering aids typically MgO, Al₂O₃ and Y₂O₃ to enhance densification of silicon nitride.

It has been demonstrated^{1,2)} that in order to fabricate high-strength, hot pressed Si₃N₄, it is preferable to start with a powder that contains a high percentage of α -Si₃N₄. During hot pressing at temperatures above 1500°C, the α -phase transforms to the β -phase via a solid/liquid/solid mechanism. The mechanisms influencing the densification of Si₃N₄ are known to be divided into three regions: the formation of a liquid phase; the α to β transformation; and the Ostwald ripening or growth of the β grains.¹⁾ S. M. Wiederhorn *et al.*³⁾ studied the strength of Y₂O₃-doped hot-pressed silicon nitride as a function of temperature, time and applied pressure. They found the behavior of Y₂O₃-doped hot-pressed silicon nitride is superior to that of magnesia-doped hot-pressed silicon nitride at 1200°C for an applied stress of 350 MPa.

E. Y. Sun *et al.*⁴⁾ reported that significant improvement in the R-curve behavior and the steady-state fracture toughness values was observed with a high Y₂O₃ : Al₂O₃ ratio in the sintering additives. They also found that silicon nitride with high Y₂O₃ : Al₂O₃ ratio such as 6.25 : 1 exhibited more extensive debonding at grain boundary interface, compared to that with low Y₂O₃ : Al₂O₃ ratios such as 4.0 : 2.8 and 5.0 : 2.0, resulting in increased intergranular fracture toughness.

The objective of the present research is to develop the pressure-assisted master-sintering surface (PMSS) of silicon nitride with high Y₂O₃ : Al₂O₃ ratio of 6.25 : 1. The PMSS is one of the hot pressing models recently developed by K. An and D. L. Johnson by extending the concept of the master sintering curve for pressureless sintering⁵⁾ in which the sintered density is a unique function of the integral value of a temperature function over time irrespective of the heating path.

2. Experiments

A dilatometer determined the linear shrinkage from the motion of the pressing ram during hot pressing.

High-purity α -Si₃N₄ powder (0.8 μ m of diameter, E-10 grade, Ube Industries, Tokyo, Japan) was mixed with 6.25% Y₂O₃ and 1% Al₂O₃. Pellets 25.4 mm in diameter and approximately 2 mm thick were pressed at 300 MPa without using binder.

Two different heating and pressure schedules were used. First, 27.6 MPa pressure was applied at room temperature and then the furnace was heated to 1800°C in separated runs at 0.083 and 0.167°C/s heating rates.

Secondly, hot pressing using applied pressures from 6.9 to 34.5 MPa were conducted. Pressure was applied at room temperature and a constant heating rate of 0.167°C/s was maintained from room temperature to 1800°C without isothermal hold.

Microstructures were examined by scanning electron microscopy on fracture surfaces. Bulk and apparent densities as well as open and closed porosity levels were determined by the Archimedes method.

3. Results and Discussion

The master sintering curve (MSC) was derived from a combined stage sintering model^{6,7)} which includes both volume and grain-boundary diffusion mechanism. The instantaneous densification rate in the latter model is

$$\frac{d\rho}{dt} = \frac{3\gamma\Omega}{kT} \left(\frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b \delta D_b}{G^4} \right). \quad (1)$$

Where γ is the surface energy, Ω the atomic volume, k the Boltzmann constant, T the absolute temperature, G the mean grain diameter, D_v and D_b the coefficients of volume and grain boundary diffusion, respectively and δ the width of the grain boundary. Γ_v and Γ_b are lumped scaling parameters.

This equation can be rearranged for either grain boundary or volume diffusion such that all terms that not explicitly functions of temperature are carried to the left hand side, and then integrated, as follows:

$$\frac{k}{\gamma\Omega D_0} \int_{\rho_0}^{\rho} \frac{G^n}{3\rho\Gamma} d\rho = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (2)$$

where Q is the apparent activation energy, D_0 is the pre-exponential term for the diffusion coefficient, R is the gas constant, and $n = 3$ or 4 for volume or grain boundary diffusion, respectively. For the master sintering curve, the measured density is plotted as a function of the right term of eq. (2), hereafter denoted Θ (See eq. (3)). If a single mechanism is responsible for densification, the sintered density can be predicted from the curve irrespective of the heating path.⁵⁾

$$\Theta = \int_0^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (3)$$

The application of MSC using silicon nitride powder was made by comparing the density of the specimens hot pressed at 27.6 MPa and heated to 1800°C in separated runs of 0.083 and 0.167°C/s heating rates. The density as a function of temperature is shown in Fig. 1.

When the density was plotted as a logarithmic function of Θ , where Θ was defined as eq. (3), the two data sets merged onto a single curve. That is a constant pressure trace on the PMSS (Fig. 2). The estimated activation energy was found to be 698 kJ/mol. This was in excellent agreement with the values in literature.^{8–10)}

The effect of applied pressure on microstructure of silicon nitride from 6.9 to 34.5 MPa was studied under equivalent heating schedule of 0.167°C/s from room temperature to

Fig. 1 Density as a function of hot pressing temperature at 27.6 MPa.

Fig. 2 Master sintering curve for data of Fig. 1.

Fig. 3 Microstructural evolution with increasing pressure (a)–(e) from 6.9 to 34.5 MPa and (f) their corresponding densities determined by Archimedes method.

Fig. 4 SEM micrographs of polished surfaces. Specimens were made at (a) 13.8 MPa and (b) 20.7 MPa.

1800°C without isothermal heating. Figure 3(a)–(f) show microstructural evolution with increasing pressure as well as their corresponding densities determined by Archimedes method.

Polished surfaces of the specimens in Fig. 3(b) and (c) show non-homogeneous densification feature of silicon nitride, since the boundary between dark and bright regions corresponding to denser and less dense regions respectively were clearly observed throughout the surface as shown in Fig. 4(a) and (b). Less dense region containing more porosity seemed bright due to the fact that electrons of scanning electron microscopy scattered more at porosity which is not electrically conductive.

Phase transformation of α to β phase was also observed while the initial powder was α phase. Figure 5(a) and (b) illustrate the X-ray diffraction patterns of the selected specimens made at 6.9 MPa and 34.5 MPa. Almost entire peaks were identified as α and β of silicon nitride. As the densification processed, the peaks from β phase increased. Although the specimen achieved close to a full density as 98.8% of theoretical, a certain amount of α phase still remained, but the exact amount is not available at this time. H. Suematsu *et al.*²⁾ reported that the phase transformation significantly depends on the types and amount of additives. They observed that the α and β phases coexist after annealing of α phase silicon nitride using $\text{MgO}_2 \cdot 3\text{Al}_2\text{O}_3$ additives; furthermore, only the β phase was found after annealing with Y_2O_3 additive. For the present study, the composition of additives were selected as 6.25% Y_2O_3 and 1% Al_2O_3 both of α and β phases were observed after sintering, which is consistent with literature.²⁾

Fig. 5 Relative peak intensities of β phase between specimens made at (a) 6.9 and (b) 34.5 MPa.

Fig. 6 Relative density versus temperature using a constant heating rate of 0.167°C/s at varying applied pressure from 6.9 to 34.5 MPa.

The density as a function of temperature for 0.167°C/s heating rate using constant applied pressures from 6.9 to 34.5 MPa is given in Fig. 6. Pressures are, from right to left, 6.9, 13.8, 20.7, 27.6 and 34.5 MPa. Figure 7 shows the constant pressure contours of the PMSS constructed from the densification data in Fig. 6. Pressures are, again from right to left, 6.9, 13.8, 20.7, 27.6 and 34.5 MPa. To develop other views, points of time-temperature integral were picked at 0.65, 0.7, ... 0.95 for each of the constant pressure curves, and multiple regression analysis was done to obtain an empirical model of PMSS. The resulting surface is shown in Fig. 8. It now is possible to predict the density of a specimen hot pressed at any pressure from 0 to 34.5 MPa if the temperature-time trajectory is known.

4. Conclusions

The application of MSC using silicon nitride powder was made by comparing the density of the specimens hot pressed at 27.6 MPa and heated to 1800°C in separated runs of 0.083 and 0.167°C/s heating rates. Silicon nitride was mixed with sintering additives of 6.25% Y_2O_3 and 1% Al_2O_3 . When the density was plotted as a logarithmic function of Θ , the two data sets merged onto a single curve, in which the activation

Fig. 7 Constant pressure contours of the PMSS constructed using the data of Fig. 6.

Fig. 8 Constant density contour plot of the PMSS.

energy was estimated as 698 kJ/mol. Phase transformation of α to β phase was also observed while the initial powder was α phase. As the densification processed, the peaks from β phase increased.

The PMSS of silicon nitride from 0 to 34.5 MPa pressure was constructed, which enables the prediction of the density if the temperature-time trajectory is known. It also can be used to specify the heating schedule required to achieve a target density at a given pressure.

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