Growth Isotherms of Liquid-Phase Sintered Silicon Nitride

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液相焼結窒化ケイ素の等温粒成長

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Grain-growth data, collected after isothermal treatment of four Si_3N_4 materials, which contained different metal oxides as densification agents, are revisited. Diffusion-controlled Ostwald ripening mechanism is generally recognized to be mainly responsible for grain coarsening upon post-densification anneal. Emphasis is placed on rationalizing the grain-growth rate in terms of viscosity of the residual intergranular glass. A simple phenomenological equation is given that allows to predict the size of the Si_3N_4 grains upon annealing process. The pre-exponential coefficient and the exponent of the equation were determined using both grain-growth and intergranular viscosity data of a model Si_3N_4 system, which contained only pure SiO_2 glass at grain boundaries. This general formulation allows to estimate the effective glass viscosity of Si_3N_4 -based materials.

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1. Introduction

Most of the liquid-phase sintered Si_3N_4 materials have good wettability with respect to silicate glasses, this being one of the dominant prerequisites for complete densification when no external pressure is applied.¹⁾ Sintering of such materials usually proceeds through three stages.²⁾ The first stage is the primary rearrangement of solid particles by liquid flow. In the second stage, the solution/precipitation process of α - Si_3N_4 takes place and the major part of the sintering shrinkage is accomplished. Moreover, a stable structure with an equilibrium morphology is formed at this stage. Then, the final microstructure is achieved by coarsening of the solid particles in the final stage of sintering, which is governed by the solution of small β - Si_3N_4 particles in the glass and their re-precipitation process onto larger pre-existing grains. Based on Kingery's model for liquid-phase sintering,³⁾ many authors have quantitatively analysed the coarsening behavior of Si_3N_4 ceramics.^{4)–6)} Among liquid-phase sintered Si_3N_4 materials, the densification behavior of a simple system containing only pure SiO_2 glass, has also been attentioned as a reference material.⁷⁾ In this model system, the SiO_2 glass stems from the oxidation process of the Si_3N_4 -starting powder upon exposure to atmosphere. Also this simply structured Si_3N_4 material seems to follow the general trend of having three distinct stages, as stated above, during its densification process. The detection of a small amount of nitrogen, which was dissolved within the grain boundary SiO_2 -glass pockets,⁸⁾ was considered as an indirect proof for the occurrence of the solution-precipitation process in this high-purity material. As we shall show hereafter, although also external pressure is necessary to achieve full density, the sintering behavior of this material can be used as a reference with respect to some elementary grain-growth parameters. In this short communication, the solution/re-precipitation mechanism will be considered, in order to describe the mechanism which drives the grain coarsening in glass-containing Si_3N_4 system with pure SiO_2 glass at grain boundaries. It is shown that, once full densification is achieved, the grain-growth rate can be rationalized mainly in terms of the viscosity of the residual glass, according to a diffusion-controlled Ostwald ripening process.

2. Experimental procedure

Four Si_3N_4 materials were sintered at 1925°C, under a N_2 pressure of 10 MPa, with the addition of different densification agents. The metal oxides added in the four materials were: (a) 5.0 mass% Y_2O_3 , (b) 5.0 mass% Sc_2O_3 , (c) 5.0 mass% $\text{Y}_2\text{O}_3 + 2.7$ mass% ZrO_2 and, (d) 5.0 mass% $\text{Al}_2\text{O}_3 + 2.7$ mass% ZrO_2 . Post-sintering isothermal heat treatment of the dense materials was performed at 1850°C for 1, 3 and 8 h under 2 MPa N_2 -pressure. Further details of the sintering and heat treatment conditions will be given elsewhere.⁹⁾ The reference material with 1.0 mass% SiO_2 as the only additive (owing to surface oxidation of the Si_3N_4 -starting powder) was densified by hot-isostatic pressing (HIPing) after encapsulation in a borosilicate glass tube.¹⁰⁾ The minimum temperature necessary to achieve full density in this material was 1950°C under 180 MPa external pressure. To monitor grain growth, HIPing was then performed for two hours at temperatures in the range of 1950–2100°C.

From all of the N_2 -gas pressure sintered materials, CF_4 -plasma-etched cross sections were prepared and analyzed using scanning electron microscopy (SEM). A Leica Quantimet 500 image-processing system was utilized for quantitative analysis of grain size. The average grain size was assumed to be simply the average grain length intercepted by a straight random line. The HIPed materials were observed by transmission electron microscopy (TEM), using a JEOL 4000EX microscope operating at 400 kV.

3. Results and discussion

SEM studies revealed a bimodal distribution of grains in all of the Si_3N_4 materials investigated. This means that generally a fraction of elongated grains of large size was found to be dispersed in a fine-grained Si_3N_4 matrix. As an example, the microstructural development of the 5 mass% Y_2O_3 -doped material in the as-sintered status and after 8 h annealing at 1850°C is shown in Figs. 1(a) and (b), respectively. It was somehow surprising that also the HIPed material with only pure SiO_2 at grain boundaries shows clear evidence of grain elongation with increasing the HIPing temperature. In fact, this material typically reveals a fine and equiaxed microstructure after HIPing at 1950°C.⁷⁾

Fig. 1. SEM images of polished and plasma-etched surfaces, which reveal the microstructural development of the 5 mass% Y_2O_3 -doped Si_3N_4 : (a) in the as-sintered status, and (b) after 8h annealing at 1850°C.

Fig. 2. TEM image of a large, elongated β - Si_3N_4 grain embedded in a fine grained Si_3N_4 microstructure, as observed in the material containing 1.0 mass% SiO_2 , which was HIPed at 2100°C for 2h.

A TEM image of one large elongated β - Si_3N_4 grain, surrounded by fine grains in the material HIPed at 2100°C, is shown in Fig. 2.

Grain-size data of the gas-pressure sintered materials could be rationalized according to a plot giving the fifth power of the average grain radius, r , as a function of the isothermal annealing time, t , at 1850°C (Fig. 3). These data are consistent with previous literature studies on grain growth in Si_3N_4 ceramics.⁶⁾ Isothermal data of the pure- SiO_2 doped material could not be collected because of both the extremely low grain-growth rate of this material and the experimental difficulty of HIPing for more than two hours. Instead, experimental data to plot the grain radius versus the HIPing temperature were collected (at a fixed HIPing time of 2h) for this pure material, as shown in Fig. 4. In the following, an effort is made to rationalize the grain-growth data shown in Figs. 3 and 4 and correlate them to each other.

Assuming that an Ostwald ripening grain-growth mechanism is effective in the present materials, the growth-rate law can be expressed as:¹¹⁾

Fig. 3. Plots of the fifth power of the average grain size, r , of four liquid-phase sintered Si_3N_4 materials as a function of the isothermal annealing time at 1850°C.

Fig. 4. Plots of the average grain size, r , of the SiO_2 containing material as a function of the HIPing temperature (holding time of 2h).

$$(2r)^n - (2r_0)^n = C_r(t - t_0) \quad (1)$$

where $2r_0$ is the average grain size at the initial time t_0 , which is the high-temperature exposure time elapsed to achieve a complete α/β transformation; t_0 , however, is assumed to be negligible in the present case; C_r is a constant that depends on the growth mechanism, and n equals 5, as experimentally determined from the isothermal data. Comparing the size of newly formed β - Si_3N_4 nuclei (typically 10–20 nm) to the average grain size observed after 1h heat treatment (i.e., 0.4–0.8 μm), suggests that the magnitude of $2r_0$ in Eq. (1) with respect to $2r$ can be neglected. This allows to consider the simplified equation:

$$(2r)^n = C_r t \quad (2)$$

where t now is simply the isothermal annealing time. When the growth mechanism is diffusion-controlled, the constant C_r can be derived as follows:¹¹⁾

$$C_r = ((8\sigma DC_0 V_m) / (9\nu RT_{ia})) \quad (3)$$

where σ is the surface tension, V_m is the molar volume, C_0 is the solution limit of the constant C_r for the case of infinitely large particles, and ν is a stoichiometric factor. R represents, in its usual meaning, the gas constant, and the absolute temperature, T_{ia} , is here the temperature of isothermal annealing. The diffusion coefficient, $D = D(T_{ia})$, in Eq. (3) is related to the viscosity of the glass, η , by inverse proportionality through a constant, α , according to the Stokes-Einstein equation. Hence, rearranging Eqs. (2) and (3) gives:

$$(2r)^n = (\theta/R) (1/\eta) (t/T_{ia}) \quad (4)$$

where $\theta = RT_{ia} C_r = (8\alpha\sigma C_0 V_m / 9\nu)$ is a constant independent of temperature, η is the viscosity of the grain-boundary

Fig. 5. Arrhenius plot of the viscosity, η , of the intergranular phase, as determined by internal friction of Si_3N_4 containing pure $\text{SiO}_2^{12)}$ as sintering aid, in comparison with data estimated from isothermal annealing (Fig. 3). The sintering agents added in various materials are explicitly shown, their respective amounts being the same as those given in Fig. 3.

ry glass at the annealing temperature, and t is the annealing time.

Equation (4) can be used to estimate the constant θ/R from the plots in Fig. 4, since the viscosity of the SiO_2 glass segregated at grain boundaries in this model Si_3N_4 material is well characterized by internal friction measurements.⁸⁾ The dependence of grain-boundary SiO_2 -glass viscosity on temperature obtained from internal friction data is shown in Fig. 5. One circumstance which strongly encourages the idea of extrapolating the value of the θ constant, as calculated from the model system, to different glass-containing Si_3N_4 materials, is that, by introducing the experimental function $\eta(T)$ (Fig. 5) in Eq. (4), the (θ/R) values calculated at different HIPing temperatures show the same value within an error of $\pm 20\%$. Furthermore, it is assumed that the physical parameters involved with the theoretical formulation of the θ constant, such as V_m , C_0 , v , α , and σ , are not, at first approximation, markedly affected either by the glass composition or by the pressure applied during processing. In other words, it is assumed here that the effect of the applied pressure plays its major role in the densification process during the primary rearrangement of the matrix grains and the solution/precipitation process which occurs in the second densification stage, while the coarsening effect, scarcely affected by it, is mainly dominated by the magnitude of the glass viscosity. Once the constant θ is determined, the viscosity of the intergranular glasses can be estimated also for the other Si_3N_4 materials, according to Eq. (4). The values found according to this calculation are plotted in Fig. 5. Consistent with the slopes of the isotherms in Fig. 3, the lowest glass viscosity is found in the Sc_2O_3 -doped material, while the most refractory glass (apart from the SiO_2 of the HIPed material) is revealed in the material that contained a mixture of $\text{Al}_2\text{O}_3 + \text{ZrO}_2$. The values of glass viscosity estimated from grain-growth measurements seem to be consistent with grain-boundary viscosity values reported in the Si_3N_4 .¹²⁾ Based on the present

data, it is concluded that Eq. (4) may be useful to predict the grain size of a wide family of liquid-phase sintered Si_3N_4 ceramics that are developed upon isothermal annealing condition, as well as more importantly to establish a rather simple technique to estimate the effective glass viscosity within newly developed materials.

It should be noted, however, that for discussing in a more comprehensive way the grain-growth behavior of some Si_3N_4 materials, one has to take into consideration the evolution of the final microstructure not solely based on the effect of diffusion-controlled Ostwald ripening. A more complete description of the process should also include the influence of nuclei formation, which will additionally affect the resulting microstructure, i.e., the final grain size. When neglecting this latter parameter, grain size is mainly governed by a diffusion process, which in turn depends on the glass viscosity. The lower the effective viscosity, η , the easier mass transport along grain boundaries is achievable and grains will grow more rapidly. A typical example is given by MgO-doped Si_3N_4 materials which, owing to the rather low viscosity of its intergranular glass¹²⁾ and according to Eq. (4) should reveal a very coarse microstructure. However, such an extensive coarsening is not observed by the experiments. Therefore, nucleation of $\beta\text{-Si}_3\text{N}_4$ during post-densification annealing has also to be considered. When, parallel to the coarsening of the microstructure, small nuclei with a size larger than the critical nuclei-size are formed, they will simultaneously grow with the other matrix grains. As a result, a refinement of the microstructure will be observed. Since it is very difficult to obtain relevant data on nuclei formation, the intention of the authors here is only to point out this additional effect, which will also alter the overall microstructure. Nevertheless, the simple experimental approach to get a rough estimate of the secondary glass viscosity in Si_3N_4 -based can be considered still valid, provided that the collected grain-growth data can be rationalized in a fashion similar to Fig. 3.

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