JOURNAL OF MATERIALS SCIENCE 10 (1975) 1169–1174

Pressureless sintering of Si_3N_4

G. R. TERWILLIGER, F. F. LANGE
Materials Science Section, Metallurgy and Metals Processing Department, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, USA

An investigation of the pressureless sintering of Si_3N_4 powder with the addition of 5 wt % MgO revealed that shrinkage by a liquid phase mechanism and bulk decomposition are two countervailing processes. Within the temperature range studied, i.e. between 1500 and 1750° C, high densities can be achieved when sintering is performed either for long periods at low temperatures or short periods at higher temperatures. A model is presented showing that pore growth due to decomposition causes a decrease in the driving force for sintering and causes shrinkage to cease.

1. Introduction

Reported attempts to pressureless sinter Si_3N_4 powders with an MgO densification aid have resulted in only limited success [1, 2], e.g. a maximum density of 80 % (based on a theoretical density of 3.18 g cm^{-3}) was achieved by Kazakov [2], but only when a large quantity (60 mol %) of MgO was added. Early attempts by the present workers were also unsuccessful and in several cases, resulted in lower sintered densities than the bulk density of the precompacted powder specimens. During these early attempts, it was recognized that the decomposition of Si_3N_4 was one of the factors limiting its sinterability, but no progress was made until a serendipitous hot-pressing experiment was performed. During this experiment, a pre-pressed disc of Si_3N_4 (+ 5 wt % MgO) was rapidly heated to 1650° C and then cooled to 1525° C prior to the application of an axial load. Although very little axial deformation resulted from the applied load, it was found that the specimen had shrunk away from the cylindrical graphite die by $\sim$ 10 % (representing $\sim$ 30 % volume shrinkage). This shrinkage could result only if a significant amount of densification had occurred prior to the application of the axial load.

Further experiments were performed to duplicate this discovery. It was found that when pre-compacted Si_3N_4 (+ 5wt % MgO) powder specimens were rapidly heated ($\leqslant$ 1 h) in a graphite susceptor to 1650° C for a period of 15 min in a stagnant N_2 atmosphere, 90 % of theoretical density could be obtained. Significantly longer periods and/or higher temperatures would result in large weight losses and lower densities. High densities could not be achieved at significantly lower temperatures. The general properties of material sintered to 90 % of theoretical have recently been reported by Terwilliger [3].

The purpose of this article is to report experiments performed in an attempt to characterize the densification behaviour and to understand the sintering phenomena in Si_3N_4. Although the effect of all fabrication parameters, e.g. particle size, amount of densification aid, impurities, etc., were not investigated, it will be shown that two countervailing processes, namely liquid phase sintering and bulk decomposition, must be considered to achieve high densities.

2. Experimental procedures

Sintering studies were performed on Si_3N_4* ($\sim$ 90 vol % α-phase and $\sim$ 10 vol % β-phase) containing 5 wt % MgO† milled 72 h in a plastic bottle containing tungsten carbide mill balls and tertiary butyl alcohol. The milled powders had an average particle size of 1.5 μm.‡ Other powder characteristics, e.g. morphology and impurities, are reported elsewhere [4]. Thin discs (0.79 cm diameter, 0.20 g weight) of the powder were pre-pressed to 60 % of theoretical density.

A horizontal induction furnace was used. As shown in Fig. 1, it consisted of a graphite susceptor with a BN inner cylinder. The sus-

---

*Advanced Materials Engineering Ltd, UK.
†Fisher reagent grade.
‡Determined by a Micromeritics particle size analyser.

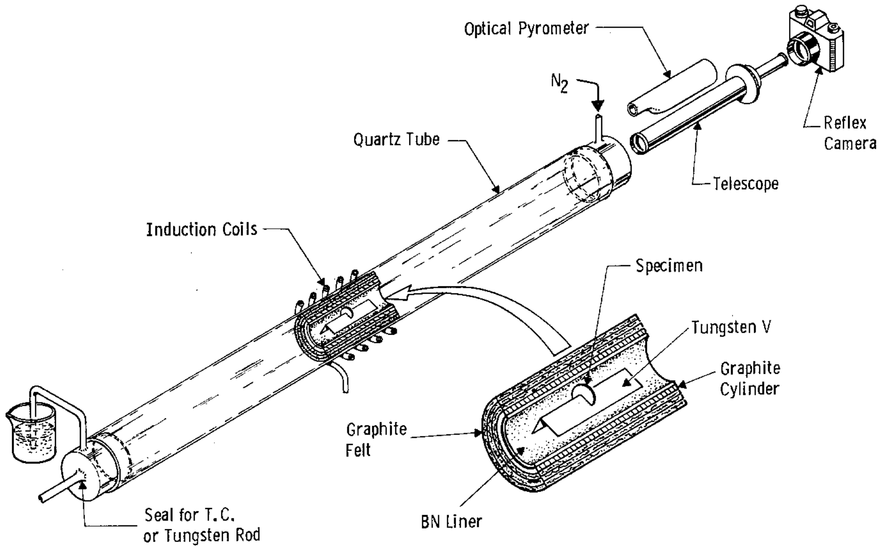

Figure 1 Furnace used for sintering studies.

ceptor was wrapped with graphite felt and contained in a clear fused silica tube through which 0.1 SCFH* of N_2 flowed. The specimen was held in a vertical position using a slotted, V-shaped tungsten holder. The temperature was recorded with a W–Re thermocouple and frequently checked with an optical pyrometer.

The specimens were photographed through a telescope to record their shrinkage as a function of temperature and time. Densities, weights and dimensions were measured after each experiment. The shrinkage of each disc specimen was determined by measuring the diameters recorded on the film negatives with a cathetometer-microscope. Final measured disc diameters and thermal expansion data for Si_3N_4 were used for calibrating the disc-film diameters.

Confirmation that the shrinkage measured in this manner was not due to the decomposition of Si_3N_4 at the disc's surface was obtained by measuring the shrinkage of the outer and inner diameter of several disc specimens containing a central hole. Shrinkage rates for the two diameters were the same within experimental error. These experiments also confirmed that the weight losses reported below were due to bulk decomposition.

Two different sets of experiments were performed:

(1) Disc specimens were heated in the furnace at a fixed, predetermined power setting. The temperature rise was relatively rapid, reaching the desired temperature within 6 to 10 min. These non-isothermal experiments were performed to determine the temperature at which shrinkage commenced and to determine the general shrinkage behaviour at different temperatures.

(2) Isothermal experiments were performed by plunging the disc specimen into the pre-heated furnace. For these experiments, the tungsten V-shaped holder was secured to a tungsten rod to allow manipulation into the furnace. Photographs were taken as soon as the telescope was focused on the specimen. After an interval of 5, 10 and 20 min, the furnace power was shut off causing rapid cooling. Besides the isothermal nature of these experiments, weight changes could be measured after fixed sintering intervals at a desired temperature.

X-ray analysis was used for phase determinations in representative specimens. Microstructures of specimens ~ 90% dense were examined with an electron microscope using etching and replicating techniques reported previously [4].

3. Results

3.1. Shrinkage versus temperature: non-isothermal experiments

The shrinkage can be divided into a low and a high temperature behaviour as illustrated in Fig. 2 for the sintering temperatures of 1605 and 1690°C, respectively. Both curves show that shrinkage begins at approximately 1300°C and

---

*Standard cubic feet per hour.

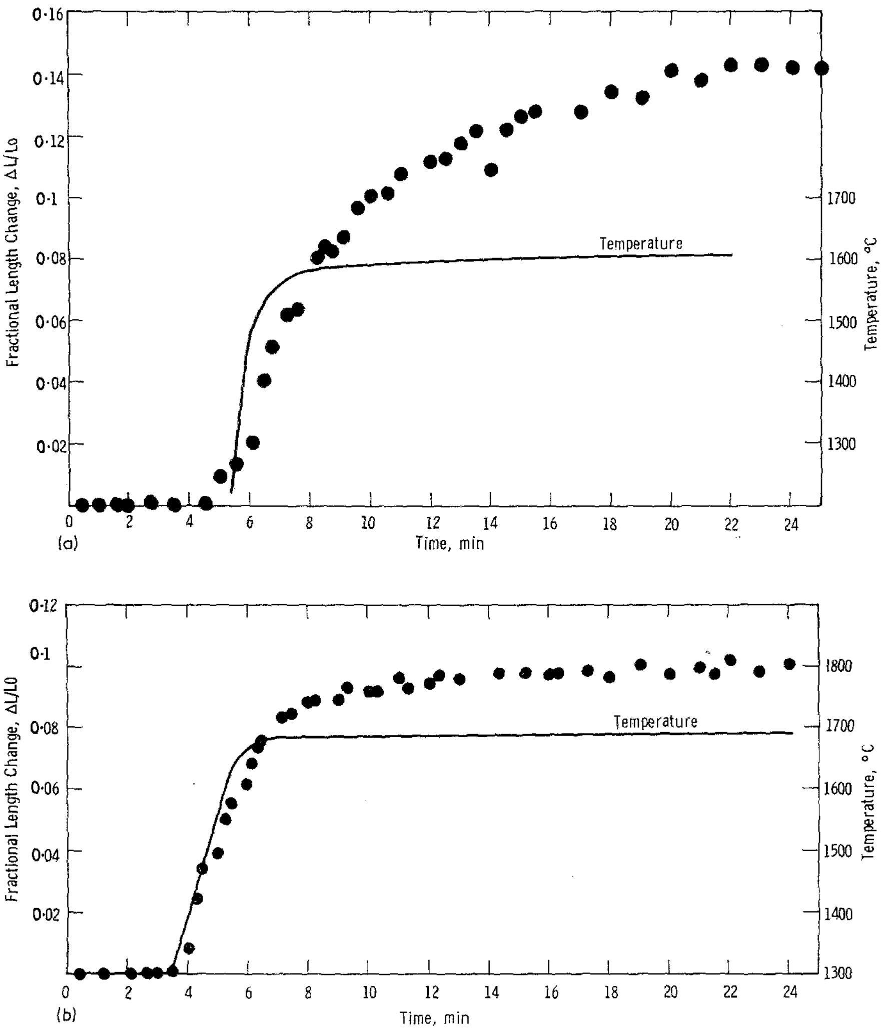

Figure 2 Non-isothermal shrinkage of Si_3N_4 (+ 5 wt % MgO) illustrating (a) low temperature behaviour and (b) high temperature behaviour.

that most of the shrinkage occurs during the relatively rapid heating. The major difference between the low (Fig. 2a) and high (Fig. 2b) temperatures is that shrinkage continued for a much longer period at the lower temperatures relative to the high temperatures.

For this type of experiment, higher densities could be obtained in the temperature range of 1545 to 1620°C; the highest was 86% of theoretical which occurred at 1570°C for a sintering period of 46 min. At 1720°C/27 min, a density of 38% was obtained, which was 22% less than the initial bulk density of the pre-compacted powder specimen.

3.2. Isothermal experiments

Densities and weight losses at the end of the three sintering periods are illustrated in Fig. 3a and b, respectively for four representative temperatures, namely 1515, 1545, 1580 and 1630°C. As shown in Fig. 3a, the highest densities could be achieved either for the longest period at lower temperatures or for the shortest period at higher temperatures. Weight losses*, shown in Fig. 3b, increased with increasing sintering period and increased temperature.

Shrinkage data (not shown) showed that most of the observed shrinkage occurred within 2 min after plunging the specimen into the hot

---

*Non-isothermal experiments conducted at 875°C resulted in a weight loss of 5% due to the volatilization of absorbed alcohol and water and possibly, the decomposition of hydrates, e.g. $Mg(OH)_2$ and $Si(OH)_4$. This 5 wt% was subtracted from all measured weight losses.

furnace. Similar to data presented in Fig. 2, shrinkage at high temperatures ceased after a shorter period relative to lower temperature shrinkage data. Due to the observed bulk weight losses, shrinkage was not always indicative of the final density.

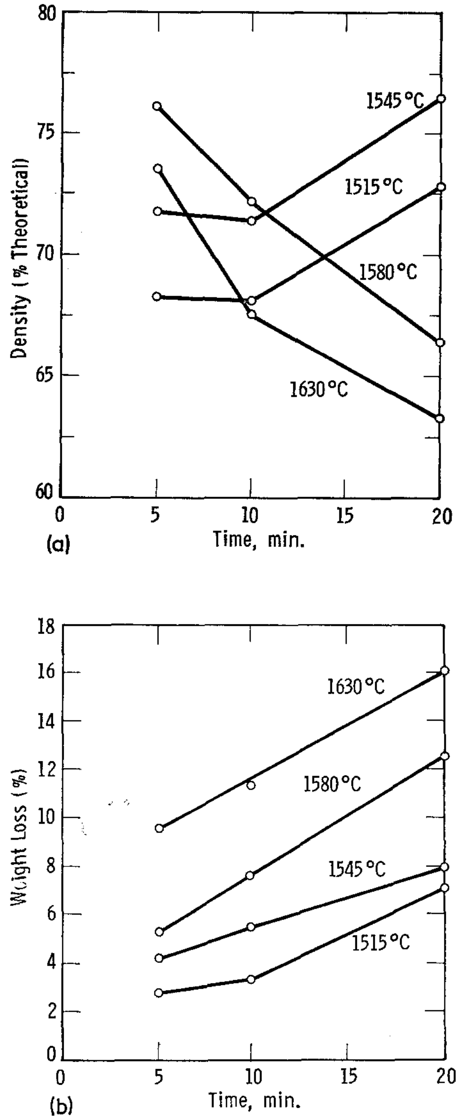

Figure 3 Densities (a) and weight losses (b) obtained for isothermal experiments at three time periods and four temperatures.

3.3. Microstructure

Both α– and β–Si_3N_4 was identified in the sintered specimens by X-ray diffraction analysis. A systematic study of the α/β ratio versus temperature and time was not performed. Free Si was not observed by this technique even for the specimens that exhibited the largest weight losses. This conclusion was confirmed by observing polished sections. The lack of free Si in the sintered specimens indicates that the observed weight losses were due to the disappearance of both Si and N_2 during the bulk decomposition of Si_3N_4.

Fig. 4 shows a microstructure of a polished, etched, 90% dense specimen in which a grain-boundary phase is easily observed (see arrows).

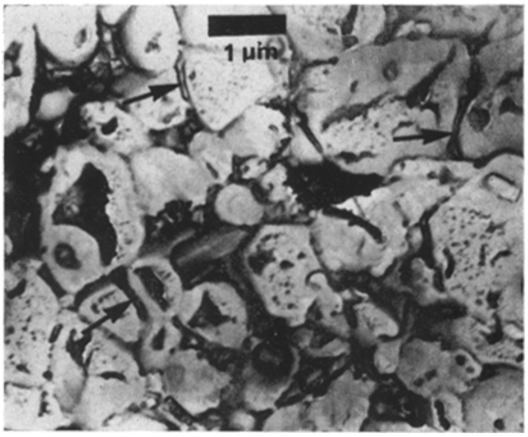

Figure 4 Microstructure of 90% dense sintered Si_3N_4. Arrows indicate suspected grain-boundary phase.

The continuity and geometry of this phase suggest liquid phase sintering, consistent with reported hot-pressing results [4].

4. Discussion

4.1. General

The most significant result of this study is that the conventional wisdom concerning the sintering of powders does not apply to Si_3N_4. This is illustrated by the fact that increasing times and temperatures do not necessarily promote increased densities.

The results reported above show that two concurrent phenomena affect the densification of Si_3N_4 (+ 5 wt% MgO) powders, namely shrinkage due to liquid phase sintering and bulk decomposition. The presence of a liquid phase is evident from microstructural observations and other reported microstructural work [4, 5]. Solution-reprecipitation due to a liquid phase has been suggested as the phenomenon leading to densification of similar powders during hot-pressing [4, 5]. Bulk decomposition is evident from weight losses at high temperatures and the studies on the decomposition of Si_3N_4 powders performed by others [6-8].

Both the non-isothermal and the isothermal experiments showed that maximum densities were achieved either at lower temperatures for relatively long periods or at moderately high temperatures for short periods. Shrinkage data from both types of experiments show that shrinkage stops after a short period at the higher temperatures where much larger weight losses are recorded. Thus, it can be concluded that decomposition inhibits the mechanism responsible for densification.

It should be noted that for comparable temperatures and sintering periods, higher densities were achieved during the non-isothermal experiments relative to the condition in which the specimens were plunged into the hot furnace. The reason for this is not fully understood but, as is evident from Fig. 2, much of the shrinkage in the non-isothermal condition occurred during heating and prior to reaching temperatures where decomposition was a major factor. This implies that the heating rate is an important factor in achieving high densities.

4.2. Sintering model

All evidence concerning the sintering behaviour of Si_3N_4 (+ 5 wt % MgO) suggest that shrinkage (due to liquid phase sintering) and bulk decomposition are countervailing processes. That is, just as shrinkage due to a sintering mechanism is indicative of pore shrinkage, bulk decomposition is indicative of pore growth.

A simple expression relating pore growth to decomposition can be obtained using the following analysis. Let $\mathrm{d}w$ be the weight of material of density ρ within the cylindrical cavity of length l between r_0 and $r_0 + \mathrm{d}r$. In this case, the cylindrical cavity represents a portion of the more complex void volume in the low density body. As defined,

$$\mathrm{d}w = 2\pi r \rho l \mathrm{d}r \,. \tag{1}$$

If this amount of material decomposes and exits to the ambient, then

$$\mathrm{d}w = 2\pi r J l \mathrm{d}t \,, \tag{2}$$

where J is the rate constant for decomposition. Equating 1 and 2 results in

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{J}{\rho} \,. \tag{3}$$

Therefore, the pore radius r can be expressed as a function of time by

$$r = r_0 + \frac{Jt}{\rho} \,, \tag{4}$$

where r_0 is the initial pore size at $t = 0$.

Since solution-reprecipitation is suspected to be the mechanism responsible for the shrinkage that occurs during the densification of Si_3N_4 (+ 5 wt % MgO) powder, one can examine the effect of pore enlargement on both the driving force and shrinkage proposed for this phenomenon. Kingery [9] has proposed the most comprehensive theoretical arguments on liquid phase sintering. He proposed that the solid particles in the three phase system (namely solid, liquid, pore) exhibit a greater rate of solubility at positions of contact with other particles. The greater solubility at these positions, which causes the approach of particle centres and thus shrinkage, is due to the capillary pressure (P) exerted by the pores on the solid particles:

$$P = \frac{2\gamma}{r} \,, \tag{5}$$

where γ is the vapour-liquid surface energy. The greater P, the greater the driving force for shrinkage.

Neglecting the decrease in pore radius due to shrinkage,* Equations 4 and 5 can be combined to show that the driving force of liquid phase sintering decreases with increasing time due to decomposition:

$$P = \frac{2\gamma}{r_0 + (Jt/\rho)} \,. \tag{6}$$

Kingery's general equation for the linear fractional shrinkage ($\Delta L/L_0$) due to liquid phase sintering as expressed in terms of the pore size (r) is

$$\frac{\Delta L}{L_0} = \frac{Kt^{1/n}}{r^m} \,. \tag{7}$$

where K is a constant and n, m are numerical exponents which depend on the rate controlling step and particle morphology (e.g. $m = 1$ or $4/3$). As assumed by Kingery, one can neglect

---

*As pointed out by Kingery [9], the change in pore radius is small for a relatively large shrinkage. For the case of the cylindrical pores considered here, a volume shrinkage of 30% corresponds to only a decrease in pore radius of only ~ 15%.

the decrease in pore size for a small change ($\leqslant$ 5%) in linear shrinkage. By combining Equations 4 and 7, the effect of pore growth on the shrinkage can be examined:

$$\frac{\Delta L}{L_0} = \frac{Kt^{1/n}}{r_0{}^m[1 + (Jt/\rho r_0)]^m}. \qquad (8)$$

Equations 6 and 8 predict that for conditions where decomposition is significant, both the driving force and the shrinkage for liquid phase sintering will cease after long periods. When this is encountered, the body will continue to decompose, resulting in a lower density. These predictions assume that the internal porosity is connected to the external surface, i.e. the bodies are $\leqslant$ 94% dense. Closed porosity would cause bloating.

The general predictions are consistent with the shrinkage, weight loss and density results reported above for Si_3N_4 (+ 5 wt% MgO) powder. Using the decomposition data reported by Batha and Whitney and assuming an initial pore radius of 0.4 μm (a reasonable value based on the initial particle diameter of 1.5 μm), their values for J at 1675°C result in a pore radius increase of 10% in vacuum and 1% in nitrogen after 60 sec. Thus, pore growth due to decomposition is significant for the temperature range studied here.

Acknowledgement

Thanks are due to our colleague, Dr F. J. Harvey for helping with the analysis on pore growth (Section 4.2). This work was sponsored by the Naval Air Systems Command, Contract No. N00019-72-C-0278.

References

1. S. AITO, S. SOMIYA and K. KATO, *J. Jap. Soc. Powder Met.* **13** (1966) 186.
2. V. K. KAZAKOV, *Trans. Izvest. Akad. Nauk SSSR. Neorganisch Materialy* **3** (1967) 1661.
3. G. R. TERWILLIGER, *J. Amer. Ceram. Soc.* **57** (1974) 48.
4. G. R. TERWILLIGER and F. F. LANGE, *ibid* **57** (1974) 25.
5. P. DREW and M. H. LEWIS, *J. Mater. Sci.* **9** (1974) 261.
6. R. D. PEHLKE and J. F. ELLIOTT, *Trans. Met. Soc. AIME* **215** (1959) 781.
7. E. A. RYKLIS, A. S. BOLGAR and V. V. FESENKO, *Soc. Powder Met.* (1969) 73.
8. H. D. BATHA and E. D. WHITNEY, *J. Amer. Ceram. Soc.* (1973) 365.
9. W. D. KINGERY, *J. Appl. Phys.* **30** (1959) 301.

Received 26 November and accepted 11 December 1974