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Microstructures of ultrafine Si_3N_4 powder compacts induced by rapid heating under controlled thermograms

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The rapid heating of ultrafine Si_3N_4 powder compacts with relatively high oxygen content was investigated with particular attention to their microstructures. The specimens were heated without resorting to additives and pressure under controlled thermograms attained by an Xe image heating apparatus. The effects of particle size and oxygen contents, as well as heating conditions, were investigated. When fired to 1700 °C within 15 s and then immediately held at 1350 °C for 10 min in N_2 atmosphere, significant densification took place in the limited region, in addition to decreasing the oxygen content to less than 0.3 wt%. This decrease of oxygen content was drastic and found to be a prominent feature of this heating process; especially, weakly oxidized ultrafine powder less than 30 nm was found to be advantageous to obtain uniform and homogeneous Si_3N_4 microstructures.

1. Introduction

Generally, covalently bonded substances are difficult to densify by conventional firing processes because of the very low diffusion coefficients of the constituent atoms [1, 2]. To date, these ceramic powders have not been densified by a conventional sintering process without resorting to additives or pressure. However, several researchers [3, 4] indicated that it would be possible to densify pure covalent materials when the starting powders are sufficiently fine and pure and when volume diffusion dominates all mechanisms. As the synthesized powders become finer and purer, however, they are more apt to be oxidized, and these oxidized ultrafine powders may also accelerate evaporation and surface diffusion at low temperature, which will cause particle coarsening at a conventional slow heating rate, and hinder densification. In this coarsening process, oxygen has been considered to be consumed in forming SiO vapour, which takes a part in the coarsening (growth) mechanism [5, 6]. Therefore, it is anticipated that heating the compacts very rapidly to the SiO evaporation temperature within a few seconds will eliminate oxygen and then immediately holding the sample at a relatively lower temperature will prevent decomposition of Si_3N_4.

In the present study, therefore, compacts of weakly and heavily oxidized ultrafine Si_3N_4 powders were heated under controlled thermograms using Xe lamp image heating apparatus, and the effects of particle size and oxygen content in the specimens on the derived microstructures were investigated.

2. Experimental procedure

The starting materials were ultrafine amorphous Si_3N_4 (about 20 nm) prepared in the laboratory by a hybrid plasma process [7]. The oxygen contents of the prepared powders increased gradually with lapse of time because of surface oxidation, as shown in Fig. 1; though the oxygen content may include the effects of adsorption of water vapour on the surface of ultrafine powder. Relatively pure ultrafine amorphous Si_3N_4 powders were more apt to be oxidized because of unstable Si–N bonding. Impurities contents have not been analysed directly: however, trace metal elements in the synthesized powders, such as Al, Fe and Ca, could be greatly minimized in the hybrid plasma system [8–10]. The characteristics of the ultrafine Si_3N_4 powders are represented in Table I. Green compacts (about 1.7 $g\,cm^{-3}$) 5 mm in diameter and 0.5 mm thick were formed at a pressure of 2.0 GPa without additives. A schematic drawing of the Xe lamp image heating apparatus consists of an elliptical reflector and a light source, as shown in Fig. 2. A transparent quartz tube (45 mm diameter and 500 mm long) surrounds the sample, and N_2 gas is passed into the tube. The thermal image heating characteristics are evaluated as follows. A 0.5 mm diameter hole with a depth 2.5 mm was bored through the side of a carbon pellet (5 mm in diameter and 1.5 mm thick). A W–5% Re and W–26% Re thermocouple was placed in the hole, in which the carbon powder was packed. The time variation of the temperature of this carbon pellet set in the BN holder was measured

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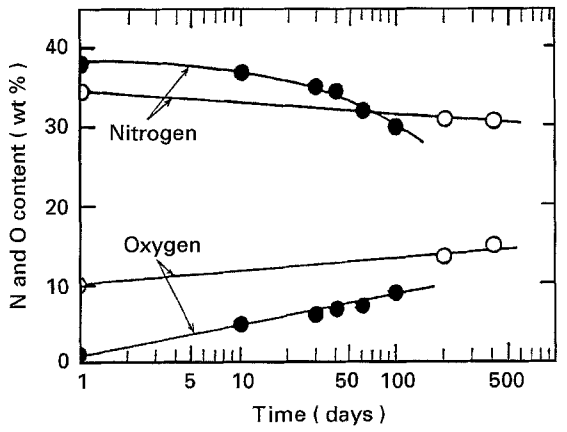


Figure 1 Nitrogen and oxygen content changes of ultrafine amorphous Si_3N_4 powder as a function of exposed time in air: (●) completely amorphous powder (N, 37 wt %; O, 2.2 wt %) and (○) partially crystallized one (N, 34 wt %; O, 10 wt %; α-Si_3N_4, 20 wt %).

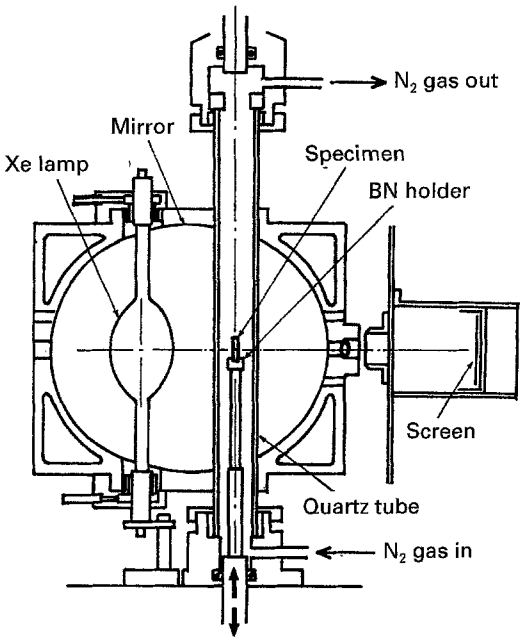


Figure 2 Schematic view of a rapid firing apparatus used for the sintering of ultrafine ceramic powders.

during irradiation, while regulating the supplied power and/or its position. As shown by Fig. 3, obtained thermograms indicate that the specimens can be heated rapidly to 1800 °C within a few seconds, as well as be held immediately at a drastically lower temperature. Here, R_0, R_1, R_2 and R_3 represent the thermograms in each case of firing to 1350, 1650, 1700 and 1800 °C within 15 s and then immediately holding at 1350 °C for 10 min. The phase of the fired compacts was determined by X-ray diffractometry (XRD) using Ni filtered CuK_α radiation. Microstructures were observed using a scanning electron microscope (SEM). A typical specimen after heating is shown in Fig. 4. For all the specimens, the most densified region, C, was taken and examined.

3. Results

3.1. Effects of heating conditions and particle sizes

To investigate the effect of heating conditions on microstructure, compacts of weakly oxidized ultrafine Si_3N_4 powder (sample 1 in Table I) were fired under thermograms, R_0–R_3. Fig. 5a–d shows SEM micrographs of the fracture surfaces for the specimens fired under thermograms, R_0, R_1, R_2 and R_3, respectively.

When the compacts were fired under thermogram R_0, only slight densification took place (Fig. 5a).

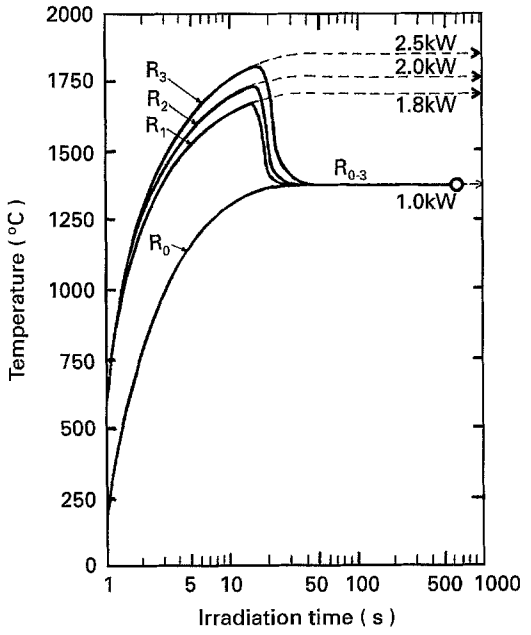


Figure 3 Thermograms as a function of irradiation time at various lamp powers. Power off: (○) 615 s.

TABLE I Characteristics of Si_3N_4 powders

Sample No.	Phase[a]	Chemical composition (wt %)					Mean particle size[d] (nm)
		N[b]	O[b]	Al[c]	Fe[c]	Ca[c]	
1	Amorphous[e]	37	2.2	< 0.003	< 0.02	< 0.005	20
2	96α/4β[f]	37	1.8	0.005	0.01	0.005	300
3	Amorphous[e]	35	15	< 0.003	< 0.02	< 0.005	20

[a] Determined by XRD.
[b] Determined by Leco analyser.
[c] Determined by atomic absorption method [8–10].
[d] Determined by TEM.
[e] Powder synthesized by hybrid plasma chemical vapour deposition [7].
[f] H. C. Starck, Germany.

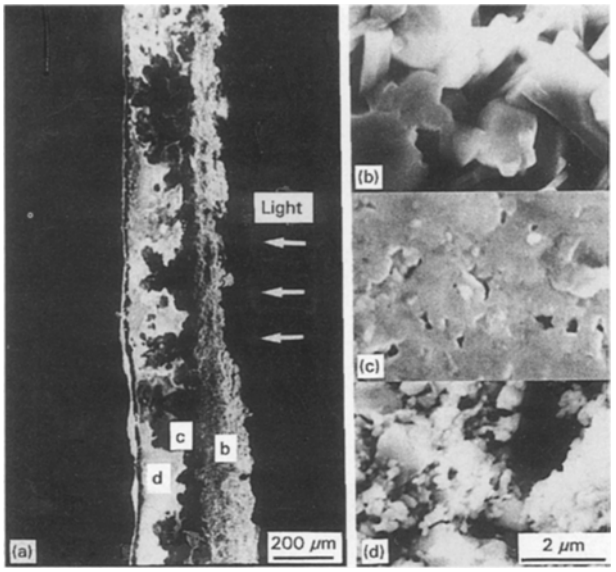


Figure 4 (a) Low magnification SEM of a typical sample. (b–d) are enlarged micrographs of regions b–d in (a).

However, the compact fired under thermogram R_1 exhibited marked densification (Fig. 5b). Furthermore, when fired under thermogram R_2, the densified pore-free domains improved (Fig. 5c). Increased densification, as shown by these results, is thought to be caused by increasing heating rate and higher soaking temperature at the initial stage. In addition, the specimen fired under thermogram R_3 showed the partial precipitation of β-Si_3N_4 crystals through liquid Si phase due to decomposition (Fig. 5d).

To investigate the effect of particle sizes on densifying microstructure, compacts of larger size Si_3N_4 powder with similar oxygen contents to sample 1 (sample 2 in Table I) were fired under thermograms R_0–R_3 respectively. As shown by Fig. 6a, b, fired bodies under thermograms R_0 and R_1 exhibit no densified microstructures. However, firing under thermograms R_2 and R_3 lead to marked densification (Fig. 6c or d). Significant deviation from the densifying behaviours of ultrafine powder compacts is clearly found by comparing Figs 6 and 5. An important observation is that the large size Si_3N_4 powder compacts are highly coarsened at thermograms R_0 and R_1 where the ultrafine powder compacts have undergone much densification. Interestingly, oxygen contents in all the specimens fired at various thermograms decreased to below 0.3 wt % irrespective of particle size.

3.2. Effect of oxygen content

The effect of oxygen content in the specimens on the microstructure was investigated by firing compacts of highly oxidized ultrafine Si_3N_4 powder (sample 3 in Table I) under thermograms R_0–R_3. Fig. 7a–d shows

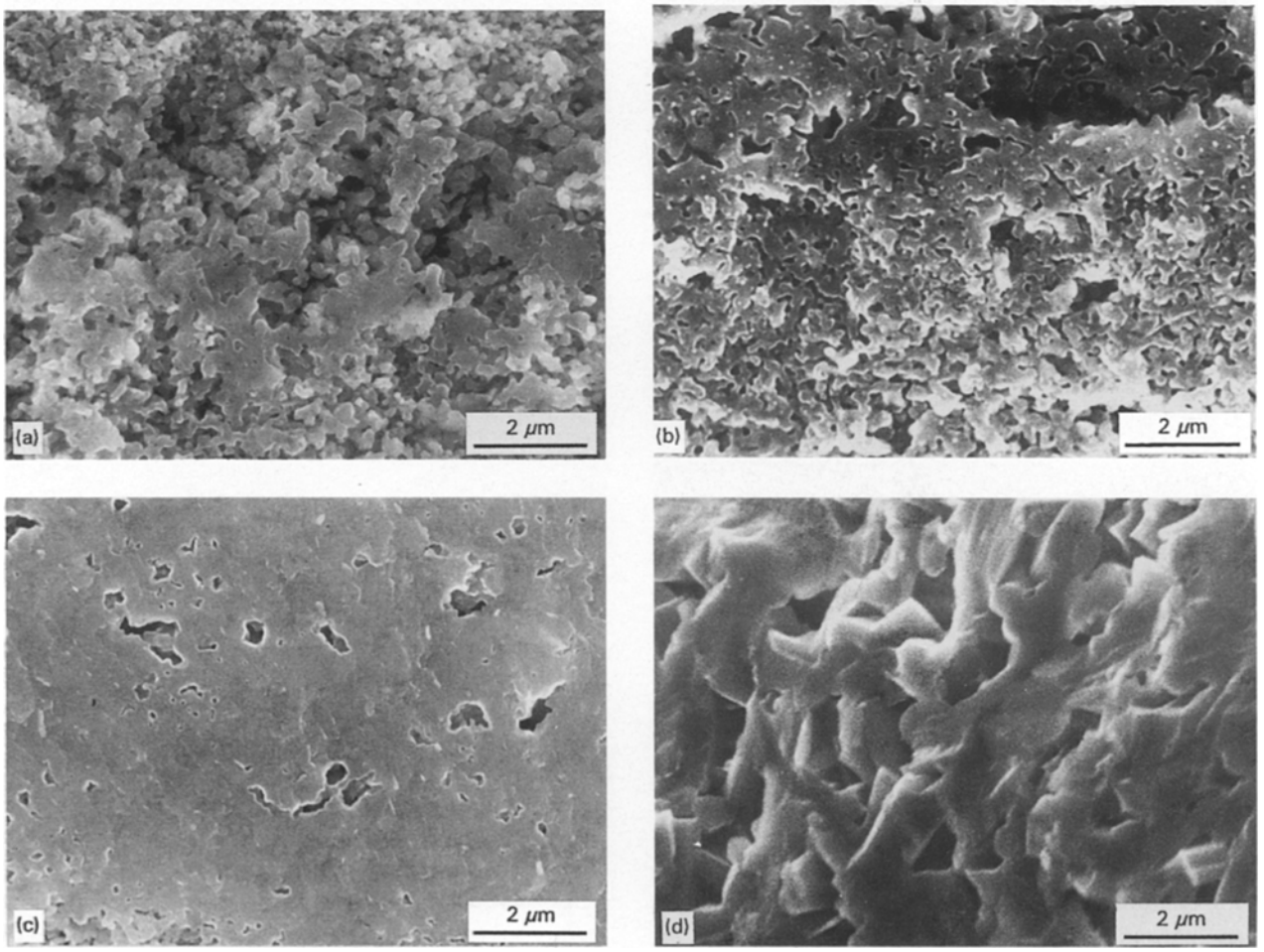
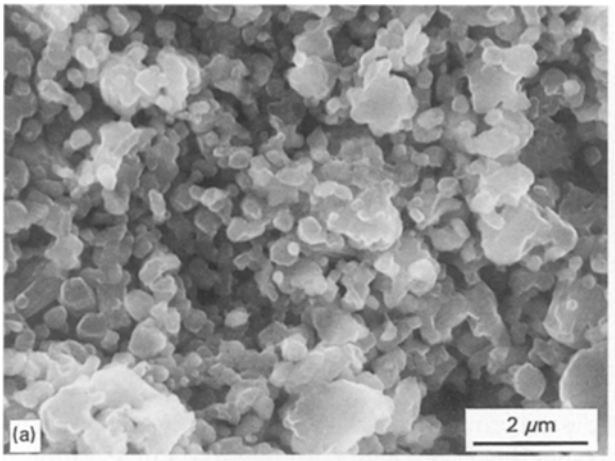
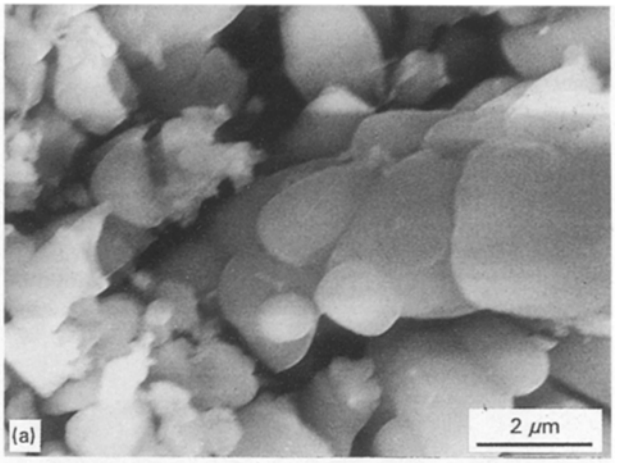
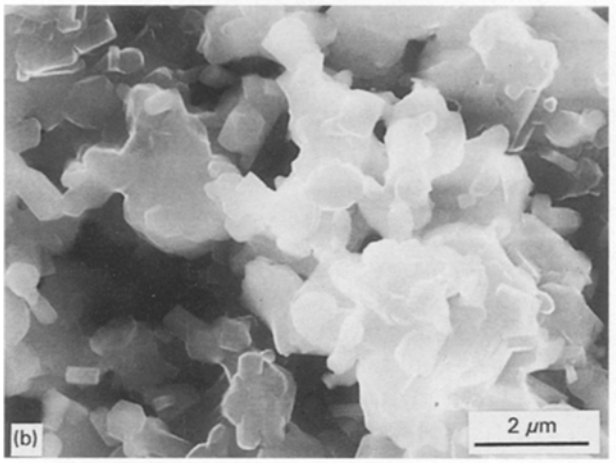
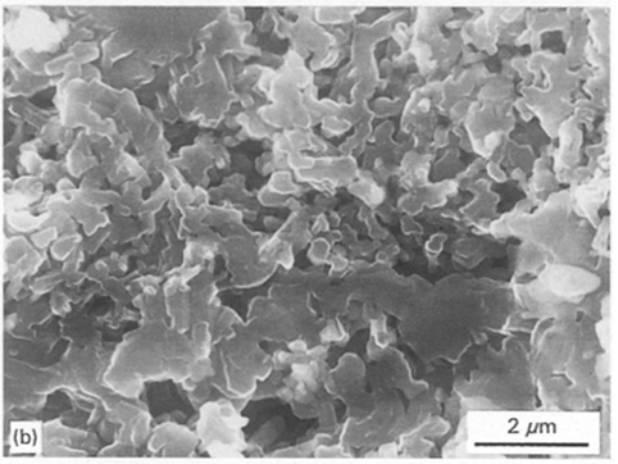


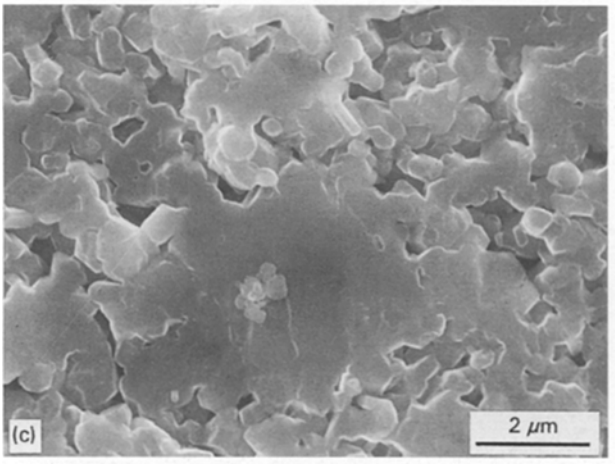
Figure 5 Effect of heating conditions on microstructure of the fracture surfaces for specimens of weakly oxidized ultrafine Si_3N_4 (sample 1 in Table I); Micrographs (a–d) correspond to those fired under thermograms R_0, R_1, R_2 and R_3 in Fig. 3, respectively.

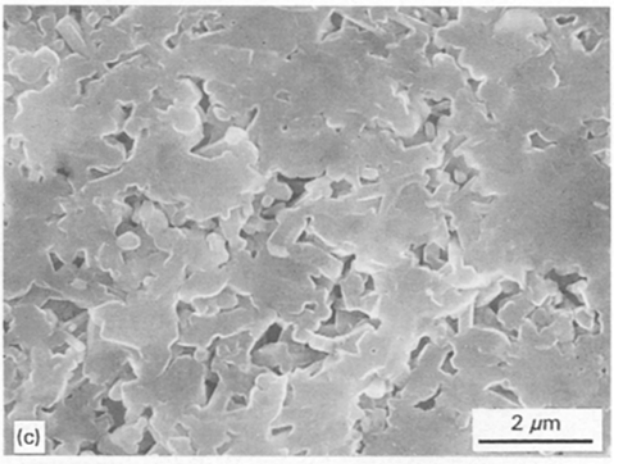


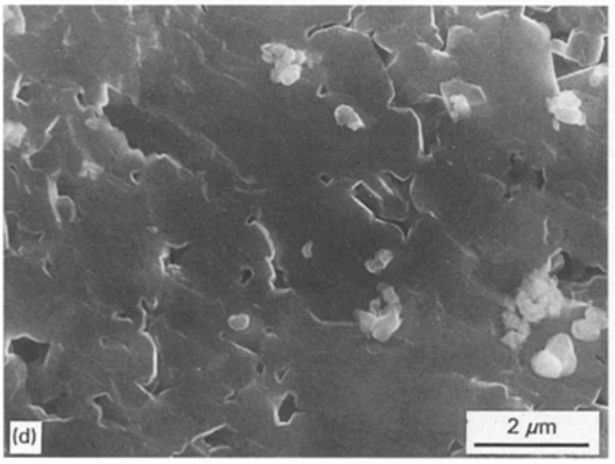












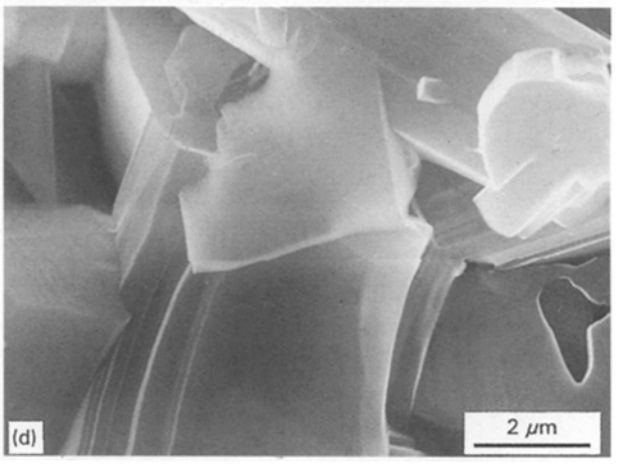


Figure 6 Effect of heating conditions on microstructure of the fracture surfaces for specimens of large size Si_3N_4 (sample 2 in Table I): Micrographs (a–d) correspond to those fired under thermograms R_0, R_1, R_2 and R_3 in Fig. 3, respectively.

Figure 7 Effect of heating conditions on microstructure of fracture surfaces for specimens of heavily oxidized ultrafine Si_3N_4 (sample 3 in Table I): Micrographs (a–d) correspond to those fired under thermograms R_0, R_1, R_2 and R_3 in Fig. 3, respectively.

SEM micrographs of the fracture surface of the specimens fired under thermograms R_0–R_3, respectively. When the compacts were fired under thermogram R_0, only α-Si_3N_4 coarsening took place (Fig. 7a). The observed formation and growth of α-Si_3N_4 is thought to be a consequence of dominating surface diffusion and/or vapour phase transport. However, compacts fired under thermogram R_1 exhibit marked densification as shown by Fig. 7b. Furthermore, when fired under thermogram R_2, densification of the compact was improved drastically (Fig. 7c). Although, the effectiveness of increasing heating rate and higher soaking temperature at an initial stage on promoting densification is noticeable in this case, coarsening phenomena due to oxygen proceed considerably as shown by comparing Figs 7a–c and 5a–c. In addition, the specimen fired under thermogram R_3 shows a rapid growth of β-Si_3N_4 crystals (Fig. 7d), which is thought to be caused by increasing evaporation rate due to higher oxygen content [8]. However, it may be noteworthy that residual oxygen contents in all the fired specimens decreased to less than 0.3 wt %, although initial oxygen contents were excessive (about 15 wt %).

4. Discussion

The use of small size powder to achieve a greater densification rate and higher final density is well established in the sintering technology of metals and oxide ceramics. For instance [11], fine size Al_2O_3 ($\sim$1.0 μm) samples could be sintered at 1150 °C to relative density >99.5%. Considering the fact [12] that diffusion coefficients of bulk Al_2O_3 decrease from 10^{-12} to 10^{-18} $cm^2 s^{-1}$ orders with decreasing firing temperature from 1700 to 1150 °C, using fine sized powders may contribute to increasing the sintering diffusion coefficients several orders of magnitude over that of the bulk powder. Similarly, it was anticipated that using ultrafine Si_3N_4 powder and heating to higher temperature may make it possible to obtain sintered bodies. To date, however, many researchers have revealed that, pure Si_3N_4 densified microstructures cannot be obtained using ultrafine oxidized Si_3N_4 powder, which may be caused mainly by particle coarsening at an initial stage. In this study, specimens with a large amount of oxygen content (Fig. 7a) or large sized particle (Fig. 6a) did not show the densified microstructures in the case of firing under thermogram R_0. However, significant improvement in the densification can be achieved by heating under thermogram R_2. This finding clearly suggests that initial heating of a specimen to 1700 °C within 15 s accelerates the evaporation of SiO and decreases oxygen content, which enhances the desired densifying transport mechanism (volume diffusion) at the holding stage.

6. Conclusions

Rapid heating to relatively higher temperature within a few second as well as holding the sample immediately at a relatively lower temperature was found to be very effective for densifying oxidized Si_3N_4 compacts with drastically decreasing oxygen contents. Using this heating process, highly densified Si_3N_4 microstructures with oxygen contents less than 0.3 wt % can be obtained using relatively low oxygen containing ultrafine powders less than 30 nm in size.

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References

1. K. KIJIMA and S. SHIRASAKI, *J. Chem. Phys.* **65** (1976) 2668.
2. F. THEUMMLER, in "Sintering process", edited by G. C. Kuczynski (Plenum Press, New York, 1980) p. 247.
3. C. GRESCOVICH and J. H. ROSOLOWSKI, *J. Amer. Ceram. Soc.* **59** (1976) 336.
4. H. J. MÖLLER and G. WELSCH, *ibid.* **68** (1985) 320.
5. S. FUTAKI, N. KUTO and K. SHIRAISHI, in Proceedings of Eighth International Symposium on Plasma Chemistry, August 1987, edited by K. Akashi (Tokyo, 1987) p. 2040.
6. J. HOJO, H. MAEDA and A. KATO, *Jpn. Yokyo-Kyokai-Shi* **96** (1988) 842.
7. H. J. LEE, K. EGUCHI and T. YOSHIDA, *J. Amer. Ceram. Soc.* **73** (1990) 3356.
8. W. X. PAN, M. SATO, T. YOSHIDA and K. AKASHI, *Adv. Ceram. Mater* **3** (1988) 77.
9. Y. TAMOU, T YOSHIDA and K. AKASHI, *J. Jpn. Inst. Metals* **51** (1988) 737.
10. W. X. PAN, PhD thesis, The University of Tokyo (1988).
11. T. YEH and M. SACKS, *J. Amer. Ceram. Soc.* **71** (1988) 841.
12. A. E.PALANDIO and R. L. COBLE, *ibid.* **46** (1962) 133.

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