Materials Science Forum Vols. 325-326 (2000) pp. 155-160

The Influence of Continuous Sintering on the Properties of Si_3N_4

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Keywords: Densification, Heating Rate, Microstructure, Fracture Toughness

Abstract

Conventional batch sintering of Si_3N_4 for commercial products is generally conducted in graphite element heated batch furnaces. Nitrogen gas pressure from slightly over atmospheric up to 100 atmospheres and the use of setter powders are typically employed to control decomposition of the parts being sintered. Generally, as the amount of sintering aid is reduced, the sintering temperatures and gas pressures are increased to reach the desired final density and physical properties.

There are several problems related to batch sintering which can have significant effects on the uniformity of properties and subsequent in-specification yield. Many of these problems can be identified as related to mass/heating rate effects and/or mass/cooling rate effects. The larger the mass, the slower are both the heating and cooling rates required to ensure uniform heating throughout the load. At typical production rates, uniform heating and cooling of large batch furnace loads are rarely achieved. In addition to these problems, the influence of the furnace atmosphere on the sintering of nitride based materials, containing oxide based sintering aids, can be quite complex. Setter powders and aged or conditioned containers are used as a means of controlling decomposition of the nitride based materials and most often have a significant effect on the surface reaction zone.

The primary goal of current research at Southern Illinois University at Carbondale, with funding from the Department of Energy, through Oak Ridge National Laboratory, and Centorr Vacuum Industries (CVI), has been to investigate continuous sintering of Si_3N_4 as a cost effective method for the commercial production of parts for the transportation industry. Under this program, a production prototype furnace was produced by CVI with a unique SiC linked belt. This furnace has the capabilities of reaching temperatures of 2000°C with a refractory metal hot zone installed and temperatures up to 2300°C with graphite hot zone installed. Using flowing nitrogen or argon to protect the hot zone and parts being sintered, allows for the continuous sintering of Si_3N_4 parts without the need for nitrogen over-pressures or special setter powders. Because the parts being sintered are continuously fed through the furnace inside BN containers, all of the parts are subjected to the same thermal history. This has significant advantages with respect to part uniformity and process yields. Also, since the heating rate and soak times are controlled by the belt speed, very high heating and cooling rates can be achieved. Numerous Si_3N_4 formulations, containing as low as 8 wt% sintering aids, have been successfully sintering to high density, strength and toughness.

This paper will provide some historical perspective on conventional sintering of Si_3N_4 and discuss past and present research results for several Si_3N_4 formulations sintered in the continuous furnace at SIU. The focus will be on the influence of the furnace environment and control on the resulting microstructures and properties.

Introduction

The open literature contains many excellent patents, conference proceedings and journal articles related to sintering of Si_3N_4 that are too numerous to cite in the allowed space. The information and techniques reported in these references have formed the basis for most of the present technologies used in the processing and sintering of the entire Si_3N_4 family of ceramics. However, with the exception of a few, many do not adequately describe the sintering equipment and environment used. The general accepted terminology for the sintering methods associated with silicon nitride are: pressureless sintering (PS), gas-pressure sintering (GPS), hot pressing (HP), hot- isostatic pressing (HIP) and reaction bonding/reaction sintering (RB).

In [1] Katz reviewed nitrogen ceramics development from 1976 through 1981. The important contributions of Greskovich, et al., Priest, et al., and Mitomo revealed the necessity to use sufficiently high nitrogen pressures to avoid decomposition of the Si_3N_4. He also discussed the use of the two-step process for sintering Si_3N_4 containing alumina and yttria sintering aids, where cladless HIPing (hot isostatic pressing) was developed. In the first step the Si_3N_4 was sintered to closed porosity at high temperature and lower pressure (~20 atm.) and in the second step the pressure was raised to much higher pressure (~100 atm.) at the high temperature. Full density was achieved by holding at elevated temperature and pressure for sufficient time to remove (or reduce) the closed porosity. HIPing and SRBSN (sintered reaction bonded silicon nitride) were also mentioned without reference to the furnace environments. Also in [1], Popper reviewed the sintering of Si_3N_4 where powder beds were used to suppress the weight loss of Si_3N_4. These powder beds have been found to create compositional gradients in the parts being sintered in them. An example was given by Popper where the reaction layer on a small part was about 2.5mm thick in an alumina-yttria sintering aid system. Woetting and Hausner in [1] sintered Si_3N_4 with and without the use of a powder bed, at temperatures up to 2000°C and N_2 pressures of 5 Mpa. The powder bed was found to result in higher part density, but weight losses were still quite high. Pompe and Carlson [1] report on sintering of Si_3N_4, employing a graphite furnace, also using the powder bed technique. They pointed out that the powder bed could provide passive protection by limiting the diffusion of gaseous products from the Si_3N_4, the sintering aids and the furnace environment. They pointed out that the carbon from the furnace environment can create a chain of self-sustaining reactions (not balanced):

$$CO(g) + Si_3N_4 \rightarrow SiO(g) + C \rightarrow SiC + O(g) \rightarrow C + O(g) \rightarrow CO(g) \qquad (1)$$

The powder bed could also be used to provide active protection by generating the same kinds of gaseous products which are generated by the article being sintered. In general, these types of powder beds are of the same composition as the article being sintered and usually form a hard non-recyclable powder encapsulation.

Hot pressing has obviously been used with excellent results to produce dense Si_3N_4 objects of simple geometry. Hot pressing also produces preferred orientation which can give superior properties perpendicular to the hot pressing direction. Expensive diamond machining is required to produce parts from these hot-pressed billets. As Jack points out in [2], the cost of machining simple spheres from hot-pressed shapes was found to be prohibitive. In [2] Saruhan, Pomeroy and Hampshire report the use of a powder bed consisting of "50% BN and 50% Si_3N_4 powder with the relevant additive combination". Even with this combination, the weight losses on sintering at 1650°C and 1 atm. N_2 were on the order of 1-2 wt%.

In [3] Boskovic et al. discuss sintering of α'-SiAlON-β-Si_3N_4 solid solutions to full density in a graphite element furnace without applied pressure. Ekstrom [3] used a submicron powder bed of BN while pressureless sintering several different SiALON formulations. O'Reilly et al. [3] also sintered α'-SiAlONs in an alumina crucible with BN packing powder using N_2 at atmospheric pressure. No mention of the furnace hot zone was made by these last two references.

Lange [4] reported sintering small cylinders from the Si-Y-O-N system using loosely packed Si_3N_4 powder in a graphite crucible. He used a tungsten element furnace which was first vacuum evacuated and then back-filled with N_2 to atmospheric pressure. During sintering the pressure was maintained at 1 atmosphere by using a pressure release valve. Similar methods have been used by others with graphite crucibles being conditioned to form an inner layer of SiC or by using SiC crucibles and mixed packing powders. Atmospheric pressure or slight overpressures of N_2 are typically maintained by bubbling the N_2 and process gases through a water column.

Presently most Si_3N_4 systems being pressureless sintered in graphite element furnaces using flowing N_2, or GPS'ed in graphite vacuum/pressure furnaces, or for very high temperature applications the parts are first sintered and then HIP'ed or two-step sinter HIP'ed in graphite element HIP's. In pressureless and GPS furnaces that parts are generally packed in setter powder in conditioned graphite boats. For conditioning, these boats have been sintered for several cycles with Si_3N_4 powder in them to convert the inner layer to SiC. This reduces the effects of Eqn. (1), but still has an effect on part uniformity and yield.

Continuous Sintering

The concept of using a continuous furnace for sintering Si_3N_4 was proposed by Linebarger, Miller and Wittmer in 1990. Some of the major advantages of sintering in a continuous furnace are:

- each part experiences the same consistent thermal history,
- heating rates and cooling rates are limitless because they are controlled by the temperature profile and the belt speed,
- heating and cooling are more efficient and thermal lag is lower because there is less free space around each part and the thermal mass of the parts is reduced,
- in-line processing is amenable to automated processing and process control, and
- improved economics are apparent for small to intermediate sized parts.

In the first continuous sintering experiments, Wittmer and Miller [5] processed A4Y13 Si_3N_4 (Si_3N_4 containing 4 wt% Al_2O_3 and 13% Y_2O_2) and sintered it in a small tungsten element belt furnace at Centorr Vacuum Industries (CVI). For comparison, material from the same lot was sintered in a small batch furnace at CVI. In both cases the A4Y13 Si_3N_4 was placed on a BN plate on top of a Mo sheet and then covered with 60/40 Si_3N_4/BN setter powder. The A4Y13 continuously sintered in the belt furnace had higher density, flexural strength, fracture toughness and Weibull than the batch sintered A4Y13.

Based on the success of the initial continuous sintering trials, SIU and CVI collaborated to obtain funding from the U.S. Department of Energy through Oak Ridge National Laboratory for the purpose of building a second generation continuous sintering furnace. This prototype furnace was designed and constructed with the flexibility to be used as a laboratory or pilot scale production furnace. The furnace was designed to use either tungsten or graphite for the heating elements (with the respective shielding) and a robust SiC link belt replaced the previous W mesh belt to allow the transport of larger loads. Flowing N_2, Ar or forming gases are used to protect the furnace chamber and product. Presently, rectangular BN crucibles with lids are used to contain the parts being sintered without setter or packing powders. Heating rate and the time at temperature are controlled by the temperature of the three independently controlled hot zones and the belt speed. For soak times of 30 min at peak temperature, heating rates of well over 150°C/min are typical for loads up to 450g. Figure 1 shows the temperature profile and heating rate for (tungsten hot zone) all three zones at 1750°C and a belt speed of 0.8cm/min. This rate would result in about 2 h at the peak temperature. Note for these conditions a heating rate maximum of about 60°C/min in a 450g load was obtained. This is well over a magnitude greater than that typically utilized in large production graphite batch furnace (usually about 5°C/min).

Following the initial work conducted using Ube E-10 Si_3N_4, compositions were also formulated with Si_3N_4 from H.C. Starck (LC10, LC12, and M11), Performance Ceramics (ASN34), Shin-Etsu, and Dow Chemical. Reduced amounts of sintering aids, the substitution of La for Y, and using BN crucibles with and without setter powders were also investigated. The procedures and data obtained are well documented in several references. [5-12] Some of the data obtained are given in Table I, which show that very high density, flexural strength and toughness can be obtained by continuous sintering. A few of the resulting microstructures are shown in Figs. 2 through 5.

Table 1 Properties of some continuously sintered Si_3N_4 formulations

Formulation	Sintering Conditions (°C min^{-1})	% Theoretical Density	4-Point Flexural Strength (MPa) (25°C/1000°C)	Fracture Toughness [13] (MPa m$^{1/2}$)
A2Y6-E10	1775/120	98.6	1068/707	6.5
A2Y6-Dow	1775/120	93.8	698/476	5.7
A2Y6-LC10	1775/120	98.1	918/---	5.9
A4Y6-E10	1750/90	100	1002/695	6.7
A4Y6-Dow	1750/90	95.7	836/506	5.7
A4Y6-LC10	1750/90	99.3	1021/---	6.7
A4Y6-LC12	1725/90	98.8	938/---	6.2
A2Y8-E10	1775/120	100	1118/767	7.3
A2Y8-Dow	1775/120	97.4	910/689	5.5
A2Y8-M11	1775/120	98.2	879/---	6.0
A2Y8-Shin-Etsu	1775/120	98.1	799/---	6.1
A2La8-E10	1725/90	99.0	995/---	6.8
A4Y6La7-E10	1700/90	99.0	982/---	6.9
A4Y13-E10	1725/90	99.8	1121/---	6.5
A4Y13-LC10	1625/90	99.5	969/---	6.5
A4Y13-ASN34	1675/90	100	1166/---	6.5

Conclusions

Several commercial formulations of Si_3N_4, SRBSN, SiAlON's, and SYAlON's have been continuously sintered (using the tungsten hot zone) with very encouraging results. In general higher strengths and toughness values and lower weight losses have been observed when compared with the commercial batch sintered results. Another advantage has been the lack of significant reaction layers which has obvious economic implications. The highest toughness ever measured by Norton for their NT451 grade was continuously sintered without the use of setter powders. Also for Norton's NT551 the continuous sintered material had higher mean strength (9%), higher Weibull (60%) and higher fracture toughness (5%). Materials from other manufacturers who wish their data and participation to remain confidential have produced similar results.

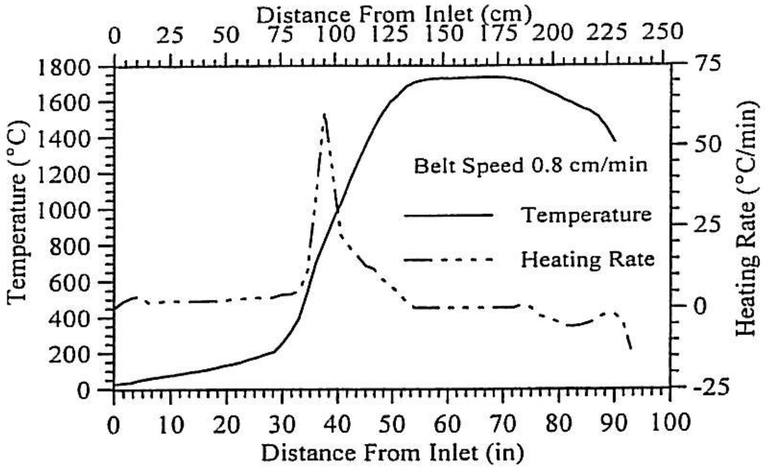

Figure 1. Temperature and heating rate for a 450 gram load using the CVI Model 44BF belt furnace at belt speed of 0.8 cm/min.

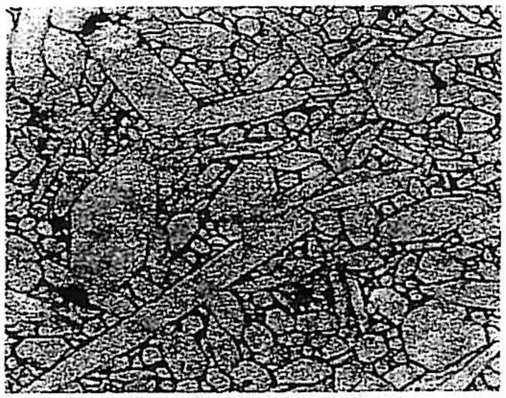

Figure 2. A2Y6-E10 (▬ 1.5 μm)

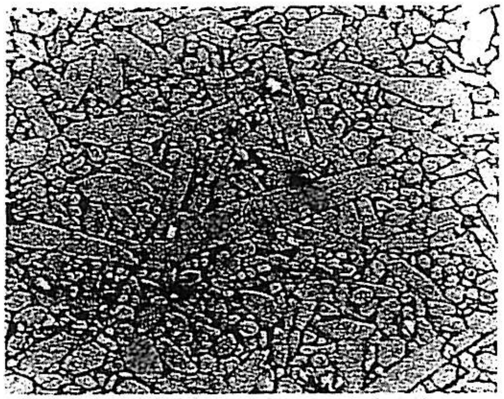

Figure 3. A4Y6-LC10 (▬ 1.5 μm)

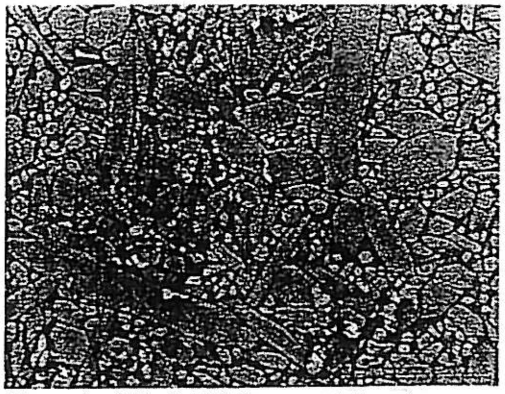

Figure 4. A2La8-E10 (▬ 1.5 μm)

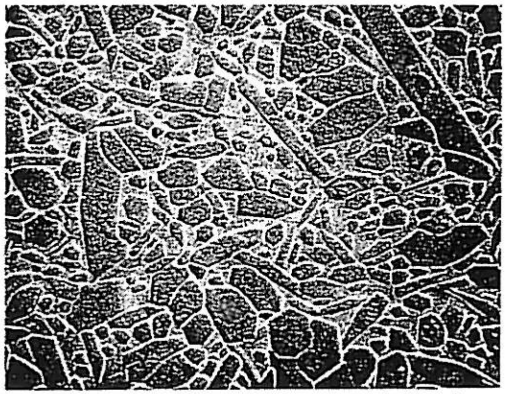

Figure 5. A4Y13-ASN34 (▬ 1.5 μm)

Previous preliminary studies using the graphite hot zone have not been as successful as those processed in the tungsten hot zone. The parts generally had higher weight loss and showed more surface reaction than those sintered in the tungsten hot zone. The initial tungsten hot zone logged over 3,000 h at temperatures from 1700°C to 1850°C prior to requiring maintenance. The graphite hot zone is currently being installed for more comparative studies and for sintering of carbides and other nitrides.

Acknowledgments

This research was sponsored by the U.S. Department of Energy under contract DE-AC05-84OR21400 with Lockheed Martin Energy Systems, Inc. Partial funding was also received from Centorr Vacuum Industries, Ind. And the IBHE-HECA-APS FY98 grant. Special thanks to H.C. Starck, Shin-Etsu, Performance Ceramics, Ceralox Corp. and Molycorp, Inc. for gratis materials used in this study.

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