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Microstructure and grain-boundary characterization of HIP'ed high-purity silicon nitride

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Laser synthesized, ultrafine silicon nitride was densified via hot isostatic pressing (HIP'ing) without any oxide-sintering-aid additions. HIP'ing was performed on *exposed* samples made from powder that had been exposed to the atmosphere, thereby picking up an oxide surface layer; and *unexposed* samples made from powders processed entirely under glove-box conditions, i.e. with minimal oxygen contamination. High-resolution transmission electron microscopy (TEM) studies indicate that the *exposed* Si_3N_4 powder samples, HIP'ed at temperatures in excess of the melting point of SiO_2, densified via a solution-reprecipitation mechanism, with an intergranular glassy phase of high-purity SiO_2. In contrast, samples of *unexposed* Si_3N_4 powder had to be HIP'ed to 2050 °C to achieve a density of $\sim 70\% \rho_{Th}$ (where ρ_{Th} is the theoretical density of silicon nitride). In this state, the sample consisted of equiaxed β-Si_3N_4 grains, with localized high-density regions. These regions had clean grain boundaries.

1. Introduction

Conventional methods of sintering Si_3N_4 involve the use of oxide sintering aids. This usually results in a glassy phase at the grain boundaries which leads to degradation of mechanical properties at high temperatures ($T \geq 1300\,°C$) due to the low viscosity of the glassy phase, i.e. enhanced slow crack growth or unacceptably high creep rates. To achieve superior high-temperature mechanical properties, it is important to control microstructural features such as: grain size and aspect ratio, grain-boundary phase chemistry, volume fraction, and crystallinity. The earliest demonstration that Si_3N_4 could be densified without the use of external oxide sintering aids was by Larker *et al.*[1] and by Honma *et al.*[2]. More recently, Miyamoto *et al.* [3], Tanaka *et al.* [4, 5] and Symons and Danforth [6, 7] have demonstrated the feasibility of densifying high-purity Si_3N_4 by HIP'ing without the use of extrinsic sintering aids. The temperatures and the pressures used were well within the practical realm of HIP'ing for engineered ceramics. Liquid-phase sintering was found to play an important role even for sintering without external additives [3–7].

In the work by Miyamoto *et al.* [3] and Tanaka *et al.* [4, 5, 8], higher impurity levels (of Al and Fe in the starting Si_3N_4 powder) allowed full densification to take place at 1900 °C, whereas 1950 °C was required for "pure" powders. In addition, strength at elevated temperatures was strongly dependent on the impurity content of the starting powders. The flexural strength of the compacts from "impure" powder was degraded above 1000 °C, whereas the strength of compacts from "pure" powders showed almost no degradation to 1400 °C [3–5]. More recently, Zeng *et al.* [9] made dense samples by HIP'ing UBE E-10 powder with up to 30 wt % additions of 99.9% pure SiO_2 powders. Their results showed that measured creep rates at 1400 °C were nearly independent of SiO_2 content up to additions of 20 wt %. The fracture strength at 1400 °C, was not significantly affected by up to 10–20 wt % of added SiO_2. These results strongly suggest that dense Si_3N_4 samples can be very refractory in nature at 1400 °C, even with significant levels of SiO_2 in the grain-boundary phase. The authors observe that this result is constrained by the requirements that the SiO_2 be very pure, and that there is not enough SiO_2 present in the grain boundaries for easy cavitation to occur (i.e. $\leq$ 10–20 wt % SiO_2 [9]).

Symons and Danforth [6, 7] were also able to densify (to 92 % ρ_{Th}) a high-purity Si_3N_4 powder by HIP'ing, and achieved good room-temperature hardness and Young's modulus values for materials with $\sim$4 wt % oxygen. While 4 wt % oxygen is higher than is typical for commercial powders, it is a normal level for powders of 16 nm diameter after exposure to

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atmospheric water vapour. It was demonstrated that at HIP'ing temperatures above 1750 °C, densification occurred rapidly via a liquid-phase solution-reprecipitation mechanism due to the presence of a liquid SiO_2 phase. Symons found that samples HIP'ed from Si_3N_4 powders with very low oxygen levels (~0.2 wt %) had lower hardness and Young's modulus values, yet these were found to be proportional to their lower densities, 69–83% ρ_{Th}. Using scanning electron microscopy (SEM) on etched samples, Symons and Danforth [6, 7] found that the final grain morphology was elongated in samples made from oxygen-contaminated Si_3N_4 powder. More recent work has shown that despite the elongated grain morphology, fracture-toughness values were low [10].

As a result of the potential high-temperature thermomechanical stability of high-purity Si_3N_4, a detailed TEM study was undertaken to characterize the microstructures of samples HIP'ed from both *exposed* and *unexposed* Si_3N_4 powders at various temperatures. After HIP'ing, samples were characterized for phase content, density, microstructure, and room-temperature properties [6, 7]. In this paper, only the microstructural development using high resolution TEM is reported. We attempted to follow grain size, morphology, neck formation, and the development of any intergranular glassy phase as a function of the HIP'ing temperature and the powders' atmospheric exposure.

TABLE I Characteristics of laser-synthesized silicon-nitride powders

Characteristics	Exposed	Unexposed
TEM (nm)	16.2 ± 2.1	
BET (ESD) (nm)	16.9	16.7
Shape	Spherical	Spherical
BET surface area ($m^2 g^{-1}$)	122	126
He pycnnometry density ($kg\,m^{-3}$)	2910	2850
Oxygen content		
neutron act. an. (wt %)	6.2[a], 4.0[b]	0.2[b]
XPS (at %)	11[a]	5
XPS N/Si (atomic ratio)	0.5777[a]	0.608

[a] Dependent on atmospheric-exposure time.

[b] After 600 °C bake-out at 5×10^{-4} Pa for 12 h.

TABLE II Trace chemical analysis of laser-synthesized Si_3N_4 powder

Element	Weight (%)	Element	Weight (%)
Cl	< 0.010	Ca	< 0.001
S	0.007	Cu	0.001
Al	< 0.001	Fe	0.001
Ta	< 0.008	Cr	< 0.001
W	< 0.008	Ni	< 0.001
C	0.072	Na	< 0.001
Mg	< 0.001	B	0.003
Y	< 0.001		

2. Experimental procedure

The silicon-nitride powders for this study were prepared by a laser-driven gas-phase reaction [6, 7, 10, 11]. The properties of these powders can be summarized as: (i) spherical and loosely agglomerated, (ii) 17 nm in diameter, (iii) stoichiometric (based on wet chemical analysis and X-ray photoelectron spectroscopy (XPS). (iv) 89-92% theoretically dense (based on He pycnometry), and (v) amorphous to X-ray and electron diffraction. The Si_3N_4 powders were processed both with (*exposed*) and entirely without (*unexposed*) atmospheric oxygen or water exposure. Table I summarizes the powders' physical and chemical characteristics, while Table II gives the trace wet chemical analysis (Luvak Inc., Boylston, MA). Samples for HIP'ing were prepared by low pressure die pressing followed by cold isostatic pressing (CIP'ing) at 350 MPa to a green density of 37% ρ_{Th}. Samples were then outgassed at 600 °C for 12 h in a 10^{-3} Pa vacuum. Samples were subsequently HIP'ed (Autoclave Engineering Inc., Model 30M, Erie, PA) in BN-lined (Union Carbide Corporation, Cleveland, OH) Pyrex® ampoules (Corning Glass Works, Corning, NY) for 1 h at temperatures from 1650 to 2050 °C at 193 Mpa. The HIP'ing procedure is detailed in [6, 7] as are the resultant properties of the HIP'ed *exposed* and *unexposed* Si_3N_4 samples.

Sample densities were measured using Hg pycnometry and the Archimedes method. Densities of > 92 % ρ_{Th} were obtained by HIP'ing the *exposed* powder compacts. *Unexposed* powders were HIP'ed to 65 % ρ_{Th} and 70% ρ_{Th} at 1950 °C and 2050 °C, respectively. After HIP'ing and removal of the glass ampoule, the sample surfaces were ground to remove any residual BN. TEM samples were prepared by mechanical polishing, dimpling, and finally by Ar-ion milling at 5 keV and 1 mA until perforation. An ISI-002B high-resolution transmission electron microscope, which has a resolution limit of 0.18 nm, was used in the observations.

3. Results and discussion

3.1. Samples HIP'ed from *exposed* Si_3N_4 powder

Earlier results [6, 7] showed that the densities of samples HIP'ed from *exposed* powder increased dramatically as the HIP'ing temperature exceeded 1700–1800 °C. It was shown that this was a result of the melting of a SiO_2-glass phase and concurrent densification via a liquid-solution-reprecipitation process. In addition, the amorphous *exposed* Si_3N_4 powders crystallized to 100% α-phase by 1650 °C. Complete conversion of the α-phase to β-phase was observed by ~1950 °C.

Figs 1–3 show low-magnification images of the *exposed* Si_3N_4 powder samples after HIP'ing under a pressure of 193 MPa for 60 min at temperatures of 1650 °C, 1750 °C and 1950 °C, respectively. The corresponding HIP'ed densities are 52, 60, and 92% ρ_{Th}, respectively. As shown in Figs 1–3, the microstructure of *exposed* Si_3N_4 samples changes significantly with increasing HIP'ing temperature. For the sample HIP'ed at 1650 °C, the Si_3N_4 particles have an average particle size of ~0.5 μm, with very little neck (i.e. small) growth between particles. The regions of Fig. 1 that appear to show neck formation are in fact regions of overlapping particles. The contrast variation observed within the individual particles indicates that bulk defects such as pores may exist inside the particles at this temperature. This defect structure may result during rapid crystallization on heating. It should also be noted that no evidence of a glassy phase was found in samples HIP'ed at 1650 °C.

Fig. 2 clearly shows that when HIP'ing of *exposed* Si_3N_4 is conducted at 1750 °C, necks are formed between most of the particles. An amorphous phase has also become visible surrounding many of the particles. This may indicate the early stages of liquid-phase sintering after 1 h at 1750 °C. The porous defect structure seen at 1650 °C is now absent. The sample density has increased to 60% ρ_{Th}, but the average particle size is still about the same as for the sample HIP'ed at 1650 °C, i.e. ~0.5 μm. This indicates that the specimen is densifying with little concurrent coarsening. At 1750 °C, the densification probably results from a combination of rearrangement, crystallization, and some liquid-phase sintering.

The sample HIP'ed at 1950 °C (Fig. 3) shows an extremely dense microstructure. The sample has now reached a HIP'ed density of 92% ρ_{Th}. Lath-like or needle-like β-Si_3N_4 grains are frequently observed, which is compatible with the proposal that the material has sintered in the presence of a liquid phase. There is clear evidence of the presence of an intergranular phase. Scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDX) work by Symons and Danforth [6, 7] showed that the grain-boundary phase contained only silicon and oxygen, (with nitrogen below the detection limit of ~ 3 wt %). It was therefore concluded that the grain-boundary phase was high-purity SiO_2. The presence of a liquid phase can clearly be observed using dark-field imaging. Fig. 4, which is a dark-field image using the diffuse scattering from the amorphous secondary phase, shows the secondary-phase as bright and the crystalline β-Si_3N_4 grains as dark. The intersections of three-grain (triple junctions) and four-grain junctions are filled with the secondary phase. A thin layer of the secondary phase is also present at the majority of grain boundaries (two-grain junctions). Fig. 5 is a

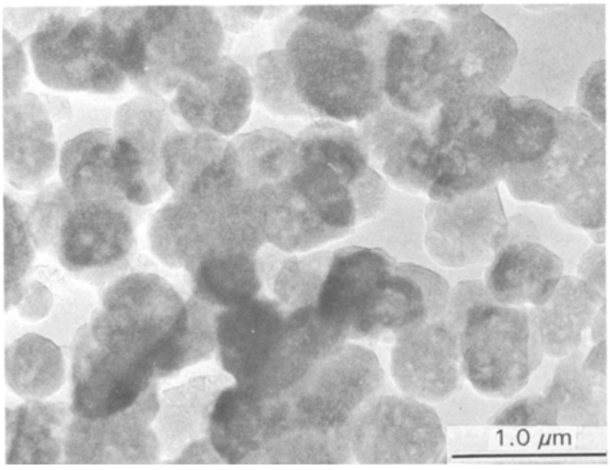

Figure 1 Low-magnification TEM image of *exposed* Si_3N_4 powder HIP'ed at 193 MPa for 1 h at 1650 °C.

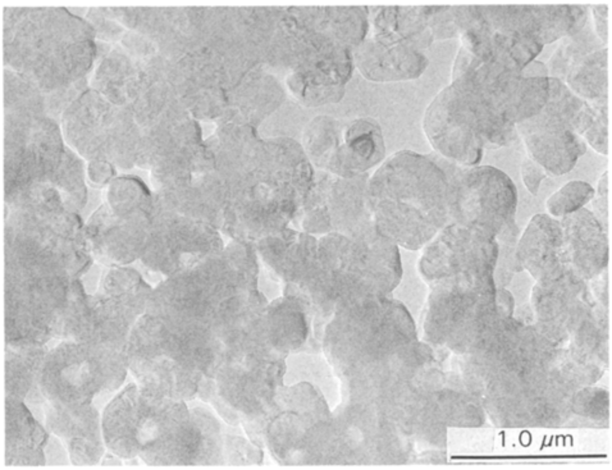

Figure 2 Low-magnification TEM image of a sample HIP'ed from *exposed* Si_3N_4 powder at 193 MPa for 1 h at 1750 °C.

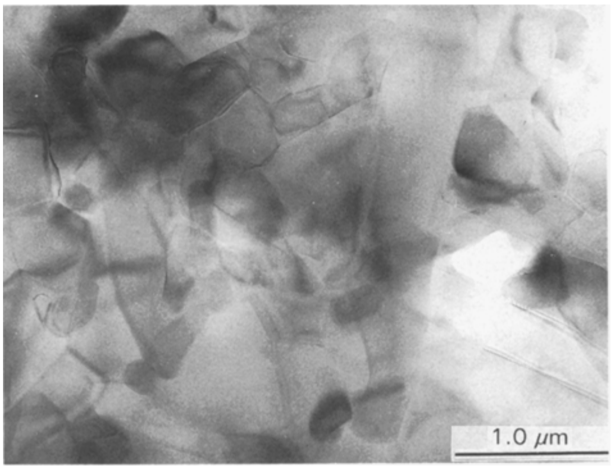

Figure 3 Low-magnification TEM image of a sample HIP'ed from *exposed* Si_3N_4 powder at 193 MPa for 1 h at 1950 °C.

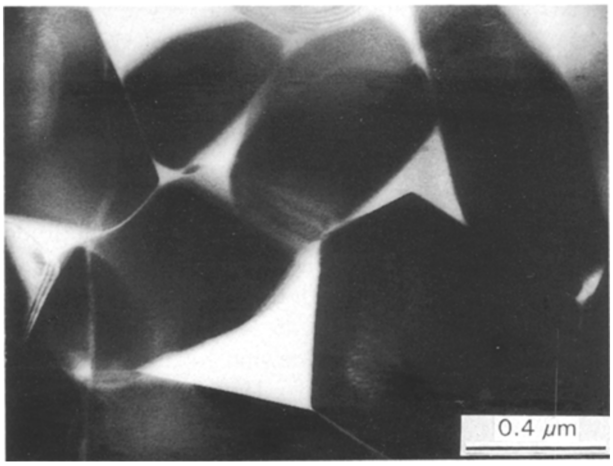

Figure 4 Low-magnification dark-field TEM image of a sample HIP'ed from *exposed* Si_3N_4 powder at 193 MPa for 1 h at 1950 °C. The image is from diffuse scattering from the amorphous SiO_2-grain-boundary phase.

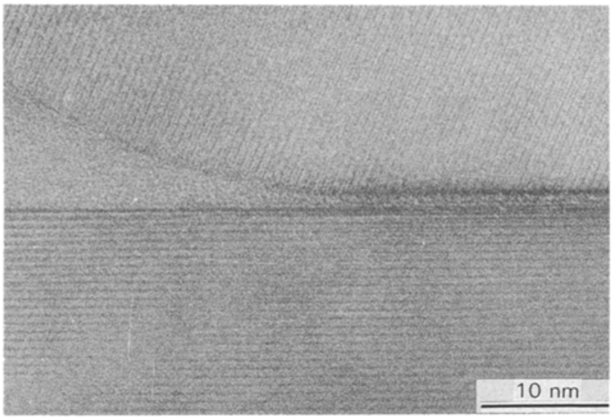

Figure 5 High-resolution TEM image of a sample HIP'ed from *exposed* Si_3N_4 powder HIP'ed at 193 MPa for 1 h at 1950 °C, showing the 1.5 nm grain-boundary glassy SiO_2 phase.

high-resolution electron micrograph showing a grain-boundary region in which the grain boundary is imaged edge-on and both adjacent grains are in strongly diffracting orientations. Direct measurement from the micrograph gave the thickness of the grain-boundary phase as 1.5 nm. The grains on the left and right are in the [$\bar{1}2\bar{1}\bar{1}$] and [$\bar{1}2\bar{1}0$] projections, respectively (i.e. the visible planes are of the {$10\bar{1}0$} type). The boundary is ($10\bar{1}0$) || ($10\bar{1}1$). The measured SiO_2 grain-boundary thickness is in fairly good agreement with the value of 1.68 nm calculated for an equilibrium Si_3N_4–SiO_2–Si_3N_4 interface by Clarke [12].

3.2. Samples HIP'ed from *unexposed* Si_3N_4 powder

Figs 6 and 7 show low-magnification images of samples made from *unexposed* Si_3N_4 powder, after HIP'ing under a pressure of 193 MPa for 60 min at temperatures of 1950 °C and 2050 °C, respectively. Sample densities were 65, and 70% ρ_{Th} respectively. An equiaxed grain morphology was observed in both samples. This is in contrast to samples HIP'ed from *exposed* powders where elongated β-Si_3N_4 grains were observed. The samples made from *unexposed* powder HIP'ed at 1950 °C still possess a relatively low average density (65% ρ_{Th}); however, locally dense regions (as high as that in the *exposed* samples HIP'ed at 1950 °C) are observed throughout the sample. These high-density regions were also observed in HIP'ed *unexposed* samples by SEM [6, 7]. After HIP'ing at 1950 °C, the average Si_3N_4 grain size is approximately 0.6 μm, and necks have formed between neighbouring particles. The sample HIP'ed from *unexposed* powder at 2050 °C shows more high-density regions than the *unexposed* sample HIP'ed at 1950 °C. The average grain size has increased somewhat to 0.8 μm.

In contrast to the samples HIP'ed using *exposed* powder, Si_3N_4 grains in samples HIP'ed from *unexposed* powders do not appear to be surrounded by any secondary phase. Dark-field images were not able to reveal the presence of any secondary phases at the triple junctions or at two-grain boundaries. The use of high-resolution TEM imaging (from the grain boundaries and triple junctions) also did not reveal the presence of any glassy or crystalline secondary-grain-boundary phases in samples HIP'ed from *unexposed* powders. Fig. 8 is a high-resolution electron micrograph showing a typical two-grain boundary for the *unexposed* Si_3N_4 sample HIP'ed at 1950 °C. The interface (two-grain boundary) in Fig. 8a is aligned nearly parallel to the electron-beam direction, while the image in Fig. 8b was obtained after tilting the crystal by ~ 2° in the direction perpendicular to the interface. The grains in Fig. 8 are in the [$\bar{1}2\bar{1}0$] projection, where the interface is of the type ($10\bar{1}0$) || ($20\bar{2}1$). A grain-boundary phase, such as was observed for samples HIP'ed from *exposed* Si_3N_4 powder, is not visible in these (or many other) high-resolution TEM images of *unexposed* samples. Thus, to at least the limit defined by the spacing of the lattice fringes parallel to the interface, i.e. 0.66 nm, no glassy-grain-boundary phase can be detected. Fig. 9 shows a high-resolution electron micrograph from a triple junction in which all three interfaces between the grains are nearly parallel to the electron beam. Since the grain boundaries in the image are not exactly parallel to the electron beam, it is not possible to conclude that there is absolutely no triple-junction glassy phase in

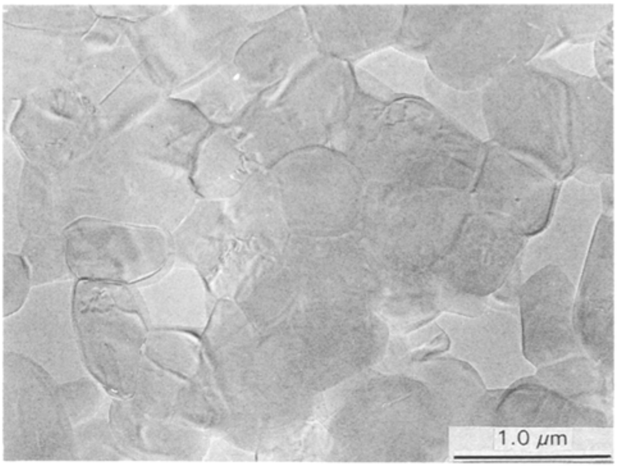

Figure 6 Low-magnification TEM image of a sample HIP'ed from *unexposed* Si_3N_4 powder at 193 MPa for 1 h at 1950 °C.

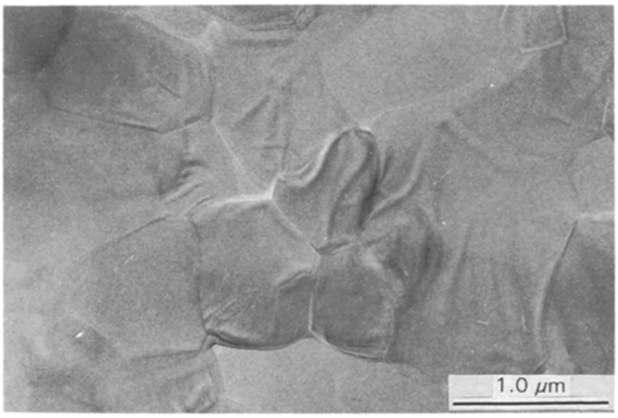

Figure 7 Low-magnification TEM image of a sample HIP'ed from *unexposed* Si_3N_4 powder HIP'ed at 193 MPa for 1 h at 2050 °C.

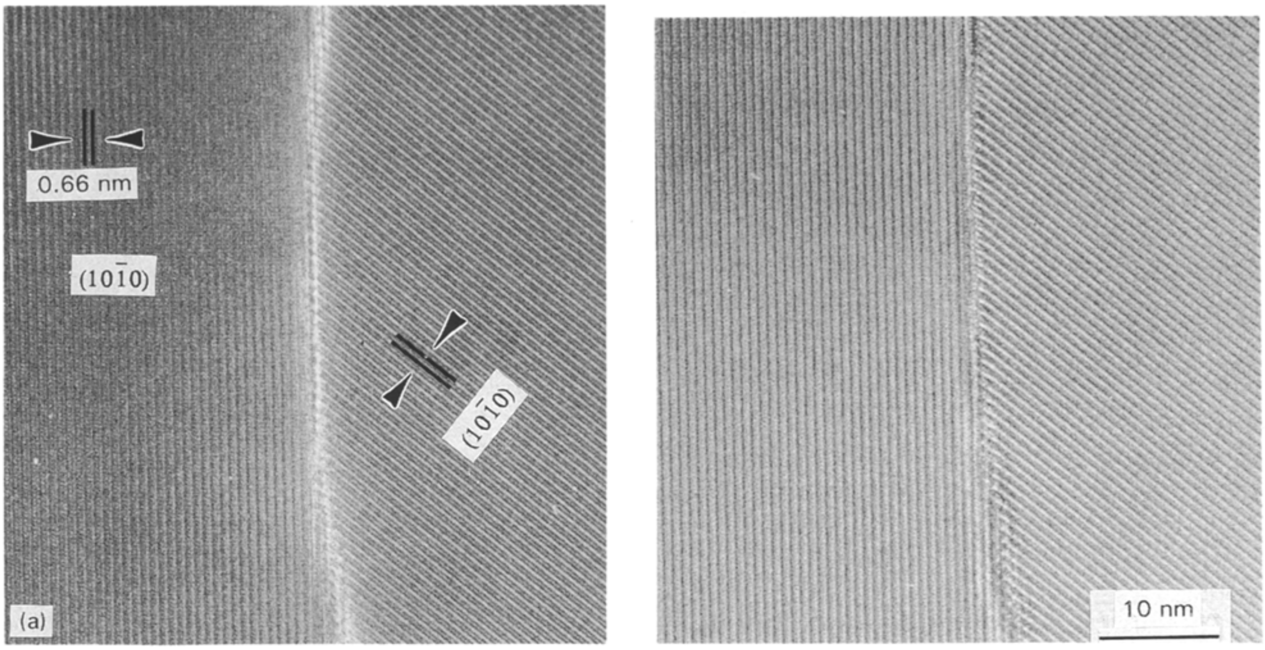

Figure 8 High-resolution TEM image of a sample HIP'ed from *unexposed* Si_3N_4 powder at 193 MPa for 1 h at 1950 °C, showing a typical clean grain boundary: (a) the boundary is very nearly parallel to the electron beam, and (b) the boundary is tilted away from the electron beam by ~2° in the direction perpendicular to the interface.

the *unexposed* Si_3N_4 samples. However, it is safe to say, based on high-resolution TEM imaging, that the glassy-grain-boundary phase as observed in the *exposed* Si_3N_4 sample is not present in the HIP'ed *unexposed* Si_3N_4 samples. Indeed, after extensive study of many such boundaries, no grain-boundary phase was detected in samples HIP'ed from *unexposed* powders.

The literature contains additional published work [13, 14] examining the interfacial characteristics in Si_3N_4 ceramics with various grain-boundary chemistries. This work points out that certain low-energy β-Si_3N_4 grain boundaries exist in densified materials which do not contain any glassy phase, even when all other higher-energy grain boundaries do contain the glassy phase at two-grain and three-grain junctions. These low-energy boundaries are reported to be of the following types: $(0001) \parallel (0001)$, $(10\bar{1}0) \parallel (10\bar{1}0)$ and $(0001) \parallel (10\bar{1}0)$. The two- and three-grain junctions shown in Figs 8 and 9 do not correspond to the low-energy types that characteristically do not contain any glassy phase. As a result, we feel confident that these clean grain boundaries are indeed characteristic of the grain boundaries in the HIP'ed *unexposed* Si_3N_4 materials used in this study.

Based on these results, one can speculate on the active sintering mechanisms for samples HIP'ed from *unexposed* Si_3N_4 powders. Certainly, some rearrangement occurs (concurrent with crystallization) during HIP'ing to 1950 °C; yet this is insufficient to explain the large, high-density regions that were observed. With no evidence of a glassy-grain-boundary phase, it is proposed that further densification occurs without liquid-phase sintering.

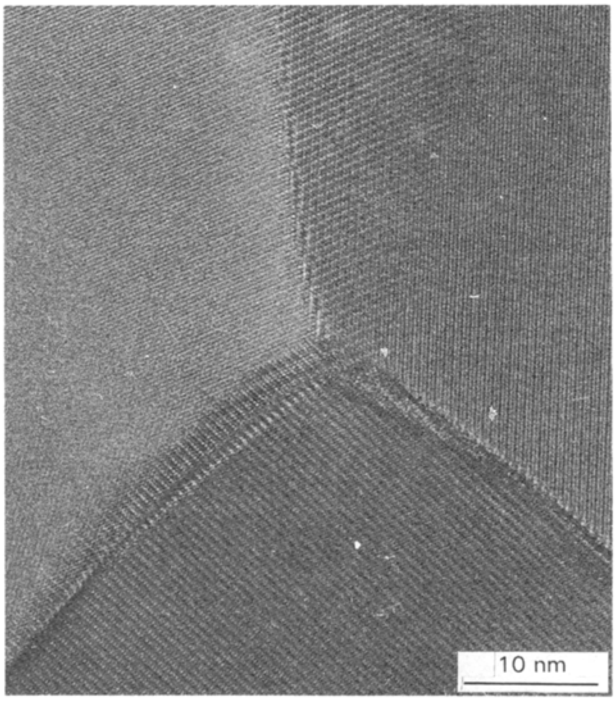

Figure 9 High resolution TEM image of a sample HIP'ed from *unexposed* Si_3N_4 powder at 193 MPa for 1 h at 2050 °C, showing a triple-grain junction.

4. Conclusion

Transmission electron microscopy of samples HIP'ed from *exposed* Si_3N_4 powder, at temperatures in excess of the melting point of SiO_2, shows microstructural evidence that is consistent with densification via a solution-reprecipitation mechanism, i.e. formation of a continuous SiO_2 grain-boundary phase and elongated β-Si_3N_4 grains. This corroborates previous observations. In contrast, samples of *unexposed* Si_3N_4 powder must be HIP'ed to 2050 °C to achieve a density of $70\% \rho_{Th}$. In this state, the sample consists of equiaxed β-Si_3N_4 grains, with both low and (locally) high-density regions. The high-density regions appear to have clean grain boundaries, i.e. no intergranular phase, crystalline or glassy, was ever detected.

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