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Kinetic aspects of superfast consolidation of silicon nitride based ceramics by spark plasma sintering†

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A newly developed novel rapid densification process named Spark Plasma Sintering (SPS) has been successfuly applied to compact silicon nitride based ceramics. In this process the precursor powders are pressed uniaxially in a carbon die, and an on–off pulsed DC voltage is applied simultaneously. The current passes through the carbon pressure die as well as the sample, so that the sample is heated both from the outside and the inside, which allows very fast heating rates to be applied (up to 600 °C min^{-1}). In addition to heat and pressure this process utilises the self-heating action caused by spark discharges between the particles, which occurs in the initial stage of the current–voltage pulse. These processes promote material transfer and allow the preparation of fully dense compacts of silicon nitride based ceramics within a few minutes. In this presentation, the phase transformation sequences during the initial stages of the sintering process, as well as the consolidation mechanisms are discussed from a kinetic point of view for Si_3N_4, β-sialon, and α–β-sialon composite materials.

1. Introduction

Spark plasma sintering (SPS) is a recently developed technique that enables ceramics to be fully densified at comparatively low temperatures and in very short times. The process itself is similar to conventional hot-pressing, *i.e.* the powder precursors are loaded in a die made of an electrically conducting material, which is normally graphite, and a uniaxial pressure is applied during the sintering process. However instead of being heated by an external source, a direct pulsed DC current is applied, which passes through the pressure die as well as the sample, so that the sample is heated both from outside and inside. This process permits very rapid heating rates (up to 600 °C min^{-1}) and fundamentally new sintering mechanisms. Originally, the inventors of the spark discharge process claimed that a plasma is generated between particles during the initial stage of the current–voltage pulse, which is why the process was named spark plasma sintering.[1] Whether or not a plasma is created has not been established yet by direct experiment. However, it is quite obvious, from various experiments carried out during the last five years, that the spark discharge generates internal localised heating, which promotes material transfer and accelerates localised reactions as well as densification.

The SPS process has been applied to compacts of varous types of material. It has been shown that silicon nitride with added liquid forming components can be compacted to theoretical density by this process in a very short time (10–15 minutes).[2,3] We have applied this technique in our previous work to compacts of sialon based ceramics. It was confirmed that, once it commences, the sintering finishes in a very short time. It was further noted that long-distance mass diffusion seems more restricted during this process, implying that the initial formation of sialon phases is more or less determined by the local chemistry, so one has to be aware that the obtained phase assemblages may be far from equilibrium.[4] As both very high heating and cooling rates can be applied, this process provides us with a new way to follow the initial phase transformations that are otherwise very difficult to follow by conventional sintering techniques, because of the unavoidable formation of transient phases. Our work was thus expanded to include compacts of different types of silicon nitride based ceramics and their composites in an effort to understand the initial phase transformation sequences and consolidation mechanisms from a kinetic point of view, as well as to tailor the microstructure and thus to control the properties.

2. Experimental

Si_3N_4 (UBE, SN-E10), AlN (H.C. Starck-Berlin, grade A), Al_2O_3 (Alcoa, A16SG) and Yb_2O_3 (⩾99.9%, Johnson Matthey Chemicals Ltd.) were used as powder precursors. Pure silicon nitride and β-sialon ($z=0.6$), and a series of silicon nitride, β-sialon and duplex α–β-sialon ceramics, with an extra addition of Yb-doped liquid-forming material, were compacted by SPS. Their overall chemical and intended phase compositions are listed in Table 1. The obtained microstructures were compared with those previously compacted either by hot-pressing (HP) or by hot-isostatic pressing (HIP).[5,6]

The SPS processing was carried out under vacuum in a spark plasma sintering apparatus, Dr. Sinter 1050 (Sumitomo Coal Mining Co. Ltd., Japan). The powder precursors were loaded in a cylindrical carbon die with an inner diameter of 20 mm. The sintering temperature was set to 1700 °C, the heating rate to 200 °C min^{-1}, and the holding time to 0 or 5 minutes. A pressure of 50 MPa was applied from the start to the end of the dwell time. The shrinkage and shrinkage rate during the sintering process were recorded, and the obtained data were corrected for the thermal expansion of the graphite punches. The set-up allows a cooling rate of 350 °C min^{-1} in the temperature range: 1700–1100 °C.

The microstructures were characterised by scanning electron microscopy (SEM) studies on carefully polished surfaces, using a JEOL 880 instrument equipped with an energy-dispersive X-ray spectroscopy (EDS) microanalysis facility (Link ISIS). Crystalline phases were determined from X-ray powder diffraction patterns obtained in a Guinier–Hägg camera, using Cu-Kα1 radiation with Si as internal standard. The unit cell dimensions of the formed phases were refined by the

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Table 1 The overall chemical and intended phase compositions of the prepared materials

		Overall chemical composition^b				
Sample	Intended phase composition^a	Yb_2O_3	Al_2O_3	AlN	Si_3N_4	SiO_2
a	α-Si_3N_4	—	—	—	100	—
b	β ($z=0.6$)	—	4.33	5.29	90.41	—
c	β-Si_3N_4 + 10 vol% L_1	13.21	—	—	85.14	1.65
d	β($z=0.6$) + 10 vol% L_2	7.50	8.49	3.89	80.12	—
e	α/β (1 : 1) + 10 vol% L_2	12.55	6.44	6.87	74.14	—

^{a}Remarks: α-sialon = $Yb_xSi_{12-4.5x}Al_{4.5x}O_{1.5x}N_{16-5x}$; β = β-sialon, $Si_{6-z}Al_zO_zN_{8-z}$; Overall composition of the extra liquid-forming materials: $L_1 = Yb_2Si_2O_7$, $L_2 = Yb_{0.25}Al_{0.5}Si_{0.25}O_{1.30}N_{0.217}$, respectively. ^{b}The chemical compositions are expressed in wt%.

PIRUM program,[7] from which the z-values of the β-sialon phases were calculated by applying the equations given by Ekström *et al.*[8] The phases present, their α/(α + β) ratio, and the unit cell dimensions of either silicon nitride or the various sialon phases formed in all samples are listed in Table 2.

3. Results and discussion

Fig. 1 shows the shrinkage curves, which reveal that no shrinkage takes place in the pure silicon nitride sample even up to 1700 °C. Once it does take place the shrinkage occurs very rapidly in all the other samples. The pure silicon nitride sample after compacting at 1700 °C is still very porous and easy to crush, and retains its original phase composition, *i.e.* the α/(α + β) ratio remains at 90% after compacting. This result indicates that although material transfer may be promoted by the SPS process, the presence of a liquid is necessary to compact a mainly covalently bonded compound such as Si_3N_4, by facilitating the α–β transformation and enhancing densification *via* a solution–precipitation mechanism.

The pure β-sialon ($z = 0.6$) sample shows a dramatic shrinkage in the temperature interval: 1400–1500 °C. Thereafter the shrinkage continues at a lower rate until the final sintering temperature, 1700 °C. With no dwell time at 1700 °C, the sample gives a density value of 2.98 g cm^{-1}, corresponding to 95% of the theoretical density. The final phase composition, as revealed by the XRD patterns shown in Fig. 2, indicates that the α–β transformation does not go to completion with such a short sintering duration (1.5 minutes from 1400 to 1700 °C). The sample is, however, already more dense than the one compacted by HIP at 1820 °C, where the α–β transformation is complete after a 1 hour hold but the density is only 87% of the theoretical density. With a dwell time of 5 minutes at 1700 °C, a fully compacted body was obtained by SPS with no noticeable residual α-Si_3N_4, implying both complete transformation and complete densification.

For the other three samples the shrinkage stops before 1700 °C, at 1670, 1580, and 1450 °C for sample c, d and e respectively, indicating that all of these samples were fully densified by 1700 °C. XRD analysis reveals, however, that the α–β transformation is not complete in sample c after sintering at 1700 °C without a hold. Approximately 43% of the Si_3N_4 remains as α-phase, but this completely transforms to β-phase after holding for only 5 minutes at 1700 °C, see Fig. 3 and Table 2. For comparison, a sample from the same batch compacted at 1700 °C for 2 hours by hot-pressing still contains 8% residual α-Si_3N_4 phase. Despite a smaller grain size, the phase composition and microstructure of samples with overall compositions of d and e, SPSed at 1700 °C with no holding time, mimic to a large extent those obtained after hot-pressing at 1750 °C for 2 hours, see Figs. 4 and 5.

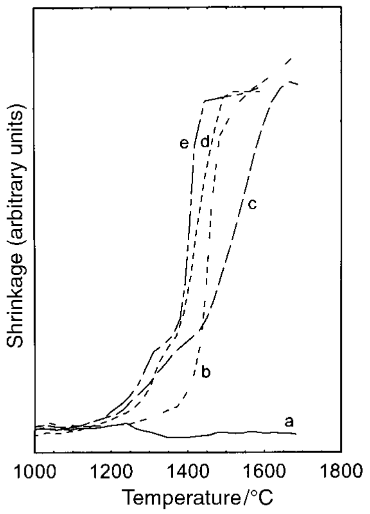

Fig. 1 Shrinkage curves recorded during SPS sintering at a rate of 200 °C min^{-1} up to 1700 °C. The curves are labelled in the same way as in Table 1.

In Fig. 1, a shoulder can be seen on the shrinkage curves of samples c, d and e before the main shrinkage takes place. This

Table 2 The formed phases and their unit cell dimensions after compacting under various sintering conditions^a

				α-phase unit cell		β-phase unit cell		
Sample	Sintering conditions	Phase assemblies	α/(α + β) (%)	*a*/Å	*c*/Å	*a*/Å	*c*/Å	z-value
a	SPS 1700 °C/0 min	α + β	90	7.755	5.620	7.605	2.907	0
b	SPS 1700 °C/0 min	β′ + α	10	7.755	5.620	7.619	2.919	0.49
	SPS 1700 °C/5 min	β′	0			7.620	2.920	0.55
	HIP 1820 °C/1 h, 200 MPa	β′	0			7.618	2.919	0.50
c	SPS 1600 °C/0 min	α + β + G	59	7.755	5.620	7.605	2.907	0
	SPS 1700 °C/0 min	β + α + G	43	7.755	5.620	7.605	2.907	0
	SPS 1700 °C/5 min	β + G	0			7.605	2.908	0
	HP 1750 °C/2 h, 30 MPa	β + α + G + $Yb_2Si_2O_7$	8	7.753	5.621	7.606	2.908	0
d	SPS 1700 °C/0 min	β′ + G	0			7.625	2.925	0.71
	HP 1750 °C/2 h, 30 MPa	β′ + G	0			7.629	2.924	0.77
e	SPS 1700 °C/0 min	β′ + α′ + G	32	7.803	5.671	7.631	2.927	0.85
	HP 1750 °C/2 h, 30 MPa	β′ + α′ + G	32	7.803	5.683	7.629	2.926	0.80

^{a}Remarks: α = α-Si_3N_4; β = β-Si_3N_4; α′ = α-sialon; β′ = β-sialon, G = a glass phase.

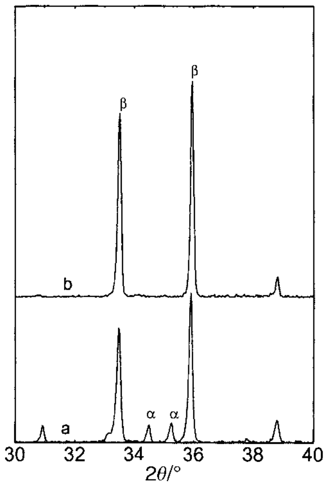

Fig. 2 The X-ray powder diffraction patterns of the pure β-sialon ($z = 0.6$) SPSed at 1700 °C with no (a) and 5 minutes (b) holding time.

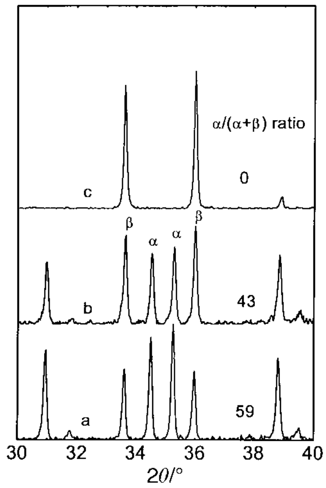

Fig. 3 The X-ray powder diffraction patterns of the silicon nitride with 10 vol% extra liquid forming material SPSed at 1600 °C with no holding (a) and at 1700 °C with no (b) and 5 minutes (c) holding time.

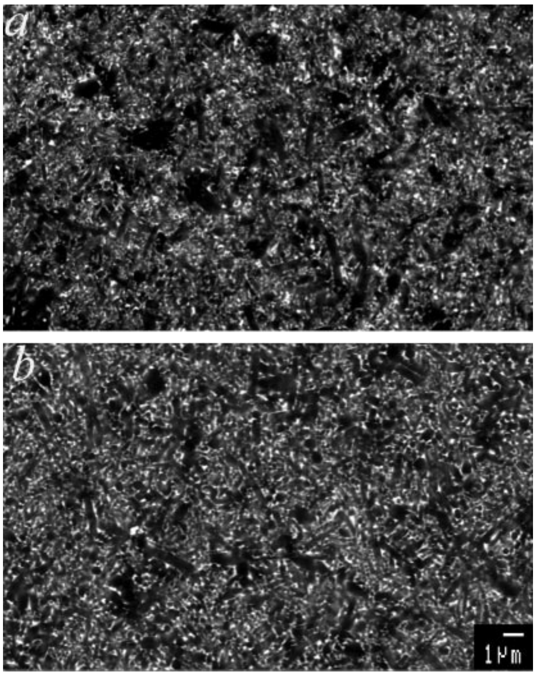

Fig. 4 Back-scattered electron scanning micrographs showing the microstructures of the β-sialon with 10 vol% extra liquid forming material SPSed at 1700 °C with no holding (a) and hot-pressed at 1750 °C for 2 hours (b). Needle-like grains are β-sialon, white spots are due to the glass phase.

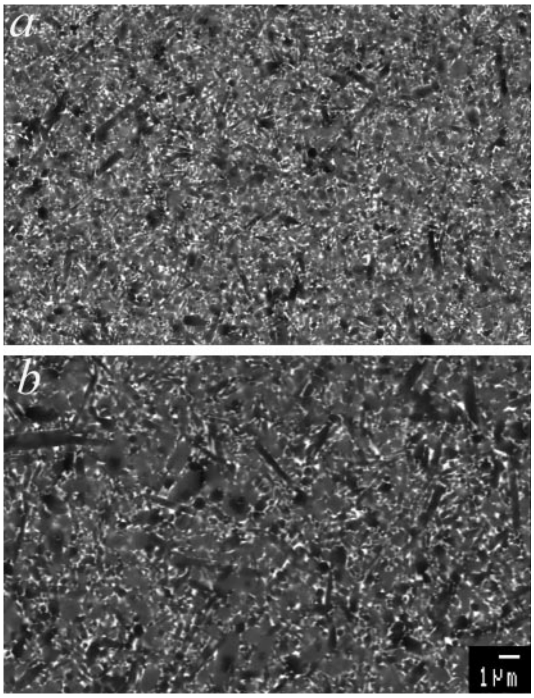

Fig. 5 Back-scattered electron scanning micrographs showing the microstructures of the α-β-sialon with 10 vol% extra liquid forming material SPSed at 1700 °C with no holding (a) and hot-pressed at 1750 °C for 2 hours (b). β-Sialon, α-sialon and glass phase have black, grey and white contrast, respectively.

most probably indicates that a eutectic oxide liquid phase has already formed at 1250–1450 °C in sample c, and 1250–1350 °C in samples d and e. It is reasonable to assume that more liquid forms when the precursor nitride powders start to dissolve with increasing temperature. Although the amount of liquid formed in these samples is designed to be similar, *i.e.*, 10% by volume, the properties of the liquid phase that forms may vary with the overall compostion of the starting powder mixtures. The liquid that forms in sample c is thus expected to be more viscous than those that form in samples d and e, because when shifting the liquid composition from the Yb–Si–O–N to the Yb–Al–Si–O–N system, both the eutectic temperature and the viscosity of the liquid are reduced. This fact may explain why samples d and e can be compacted at a comparatively much lower temperature.

Once a liquid phase is formed, densification progresses very fast in the SPS process. In the simplest case of Si_3N_4 doped with 10 vol% liquid-forming material (sample c), the sample is already fully densified at 1600 °C, although at this stage the α–β transformation is far from complete, and the liquid phase is not distributed evenly through the sample due to the lack of diffusion, see the SEM picture shown in Fig. 6. It can also be noticed in this figure that the grain growth is tremendously fast. Thus, the average size for sample c compacted by SPS at 1700 °C for 5 minutes is even larger than for the sample from the same batch compacted by hot-pressing at 1750 °C for 2 hours.[5] This seems to indicate that the grain-coarsening in SPSed samples is more likely to be controlled by interface reactions, rather than by diffusion.

4. Conclusions

In summary, the present work shows that various types of silicon nitride based ceramics can be compacted to full density

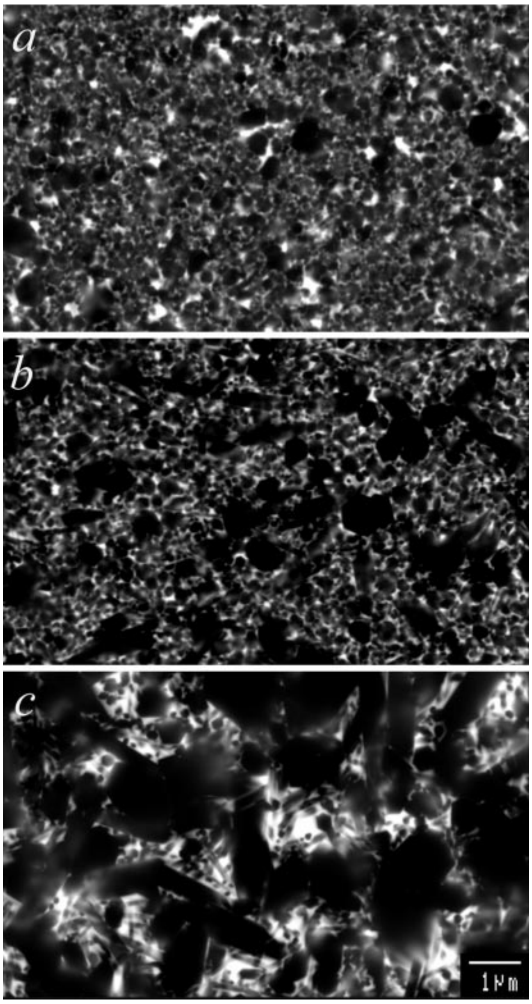

Fig. 6 Back-scattered electron scanning micrographs showing the microstructures of the silicon nitride with 10 vol% extra liquid forming material SPSed at 1600 °C with no holding (a) and at 1700 °C with no (b) and 5 minutes (c) holding time.

by the SPS process at lower temperatures and with substantially shorter holding times than required for hot pressing or HIP. It is confirmed that the formation of a liquid phase is necessary to facilitate the α–β transformation and enhance densification *via* a solution–precipitation mechanism. The phase assemblages in fully compacted bodies, however, may be far from equilibrium due to the very fast consolidation. This opens up new possibilities to tailor the microstructure; the $\alpha/(\alpha+\beta)$ ratio, grain size, as well as grain morphology can be changed by simple variation of the SPS sintering parameters. On the other hand, one has to be aware that some SPSed materials are metastable, implying that the materials may later approach equilibrium, changing their microstructure and properties, especially during service at higher temperatures. The grains grow so fast during the SPS process, that diffusion-controlled grain growth mechanisms proposed for traditional liquid-sintering seems not fit to the present observations. The grain-coarsening in SPSed samples seems to be controlled more by interface reactions.

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