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Synthesis, sintering and characterisation of TaON materials

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Abstract

Theoretical investigations predict that TaON is likely to possess a relatively high hardness, thus making it a candidate for application as an abrasive or cutting tool material [J.E. Lowther, Theoretical study of potential high pressure phases of TaON and quaternary $ZrTaO_3N$, in press]. TaON powder was produced by nitridation of amorphousTa_2O_5 powder in flowing ammonia in the 700–900 °C temperature range and an ammonia flow rate range of 40–50 cm^3/min. The resulting powders were characterised in oxidation resistance by thermo-gravimetric analysis (TGA), phase purity by X-ray diffraction (XRD) and surface area by the BET method. The materials were densified under pressure using a belt type high pressure apparatus at 3–5.5 GPa in the temperature range of 920–1200 °C. The sintered samples were characterised in phase purity, Vickers macro-hardness and fracture toughness.

Keywords: A. Sol–gel processes; A. Sintering; C. Hardness; E. Cutting tools

1. Introduction

In recent years there has been increased research in transition metal oxynitrides. Tantalum oxynitride is no exception in this regard. This has emanated from the possibility of attaining attractive properties such as high thermal, chemical stability and good mechanical properties [2–5]. Tantalum oxynitride is a candidate for applications which include nontoxic paint pigments, catalysis, future use in the electronics industry and as a possible cutting tool material [1–6]. Theoretical calculations have shown a high bulk modulus value and therefore it could be a possible candidate for cutting tools [7]. Synthesis of TaON has been achieved through a partial substitution of oxygen in an oxide precursor compound by nitrogen using an ammonia flow method at elevated temperatures [4,8–11]. Tantalum in the oxidation state V can form two ionic-covalent nitride type compounds, Ta_3N_5 and TaON [5]. TaON has the same ambient monoclinic structure as ZrO_2. The formation of TaON has been found to occur intermediate between the oxide precursor Ta_2O_5 and the fully nitrided phase, Ta_3N_5. From literature the enthalpies of reaction for the formation of TaON and Ta_3N_5 are ~9.25 and ~610.00 kJ/mol at 298 K, respectively [5]. Under dry ammonia TaON formation is controlled by kinetics, and is formed in a mixture with Ta_3N_5 or Ta_2O_5. To synthesise pure TaON instead of Ta_3N_5 the use of water vapour pressure in the ammonia according to the equilibrium:

$$3TaON + 2NH_3 = Ta_3N_5 + 3H_2O \quad (1)$$

is favourable.

Attempts have been made to produce TaON thin films by magnetron sputtering and pulsed laser deposition on various substrates by several authors [4,8,12]. A pressure-induced transition has been reported to occur at ~30 GPa into a higher symmetry nine coordinated cotunnite phase [13]. There have been speculative reports on the potential high hardness value of this high symmetry cotunnite phase [1]. There exist no data concerning the properties of TaON-ceramic materials. Therefore, in the present work a study was undertaken to prepare TaON powder and to evaluate sintering conditions for obtaining well-densified TaON materials. The properties of the densified materials were compared to those of ZrO_2 ceramics.

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2. Experimental

2.1. Precursor synthesis

A sol–gel method was used to obtain active oxide precursors. Twenty-five grams of 99.999% $TaCl_5$ (Aldrich) were dissolved in calibrated amounts of absolute ethanol (Aldrich) in a dry box and the mixture stirred for about 15 min. The beakers were sealed with parafilm and removed from the dry box. The mixtures were hydrolysed with de-ionised water by a drop wise injection method with continuous stirring at room temperature. The gel was aged at 80 °C for 24 h. The gel was oven dried in air at 100 °C for 12 h followed by subsequent milling with 4 mm steel balls at 250 rpm for 4 h in a planetary mill, washing in absolute ethanol and calcination in a muffle furnace at 600 °C for 6 h.

2.2. Characterisation of oxide gel

The oxide gel was characterised in thermal decomposition in air by thermo-gravimetric analysis (TGA) at a heating rate of 10 °C/min up to 1000 °C. The calcined powder was analysed for residual chloride by EDX (energy dispersive X-ray) with a Philips XL-30 SEM. The microstructural morphology of the powders was revealed by SEM and the particle size estimated by particle size analysis with a Mastersizer 2000. The surface area of the powders was determined by the BET method.

2.3. Thermal nitridation

In order to obtain the oxynitride phase, oxide precursors were thermally nitrided in flowing ammonia (99.99%) with an ammonia flow rate range of 20–50 cm^3/min, ammonolysis times of 60–360 min and to different final temperatures at a heating rate of 10 °C/min in a tube furnace with a silica tube of length 1200 mm and external diameter of 40 mm. Gas connections to the tube were provided by glass fittings. The water vapour pressure was realised by bubbling the ammonia through a water bath at room temperature prior to supply to the furnace. The water vapour pressure of such a set up was approximated to be $\sim 3.1 \times 10^3$ Pa [14]. Approximately 2 g of powder were placed in an alumina boat for each run. The samples were allowed to cool to room temperature under flowing ammonia.

2.4. Characterisation of TaON powder

The TaON powder was analysed for nitrogen and oxygen using an ONH Eltra 2000 analyser on at least three different samples. Phase purity determination was carried out using X-ray diffraction with a Philips PW1830 diffractometer operating with Cu Kα radiation using a step scan of 0.020° recorded in a 2θ regime of 10–80° for 1 h 30 min. Thermal stability of the powder in air was studied using TGA (thermo-gravimetric analysis) at a rate of 10 °C/min up to a final temperature of 1000 °C using a Perkin-Elmer TGA 1. Particle size analysis and morphology of the raw powder were done using the Mastersizer 2000 and SEM, respectively.

2.5. Sintering and materials characterisation

TaON powders were compacted to green pellets and capsulated in 17 mm Ta alloy cups, outgassed in vacuum and sealed at 715 °C using an In/Ag alloy. The powders were sintered under vacuum using a belt-type high-pressure apparatus in the temperature range of 920–1200 °C in a pressure regime of 3–5.5 GPa for periods of up to 30 min. The sintered samples were characterised for phase purity by X-ray diffraction. Vickers hardness (HV10) was measured by averaging five-point measurements under a load of 10 kg applied for 10 s. Fracture toughness, K_{IC} was determined by an indentation fracture method using a load P of 10 kg for 10 s using equation by Shetty et al. [15].

3. Results

3.1. Synthesis and properties of TaON

The oxide powder exhibits a large surface area with granule formation (Fig. 1). BET results reveal a surface area of 6.60 ± 0.02 m^2/g. Analysis of the gel by EDX in SEM revealed some residual Cl^- ions owing to the use of $TaCl_5$ precursor. No residual chlorides were present after calcination at 600 °C. At this temperature it is predicted that all the alkyl group organics and chlorides would have been driven off (Fig. 2). For the preparation of the TaON powder the temperatures, time and flow rate of ammonia were changed systematically. The results are summarised in Fig. 3 and Table 1.

The samples which were nitrided at 700 °C showed single phase Ta_2O_5 (XRD) for all ammonia flow conditions. A white coloured powder was obtained in all cases. Single phase Ta_2O_5 was also obtained during nitridation at 800 °C at flow rates $\leq$40 cm^3/min. A green-grey sample with clearly visible white specks was observed on increasing the flow rate to 50 cm^3/min. X-ray diffraction of this sample showed some biphasic character with both Ta_2O_5 and TaON peaks present. The nitridation at 900 °C and flow rates of 20–30 cm^3/min resulted in mixtures of Ta_2O_5 and TaON. Single phase ‘‘olive green’’

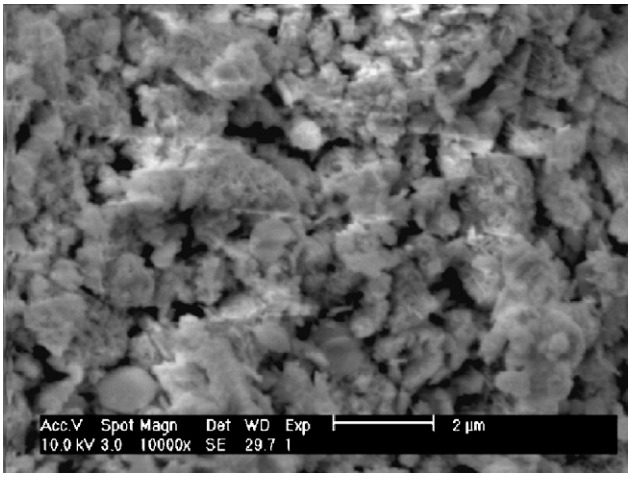

Fig. 1. SEM micrograph of Ta_2O_5 powder calcined at 600 °C for 6 h.

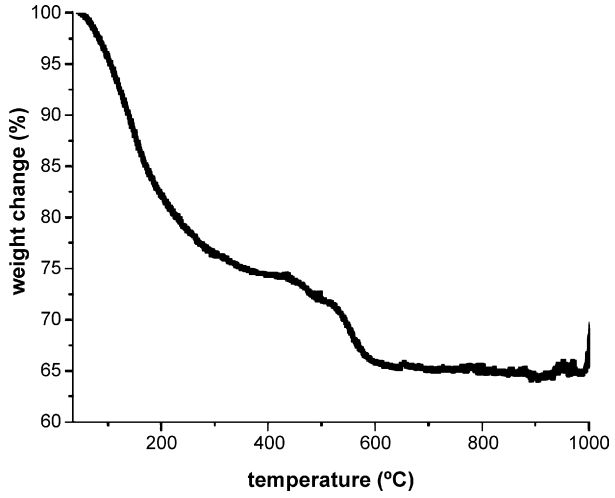

Fig. 2. TG curve for the thermal decomposition of the Ta_2O_5 gel in air.

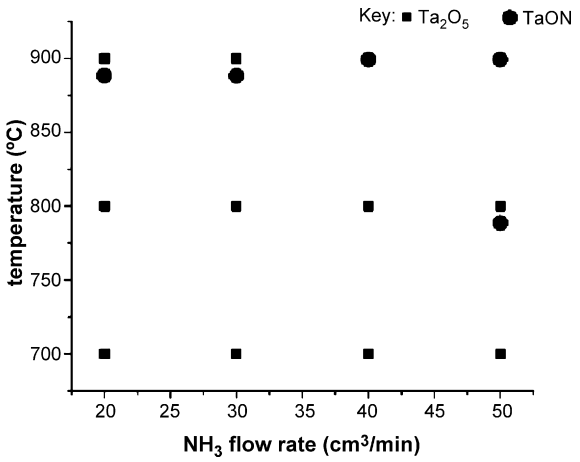

Fig. 3. A representation of the observed phases prepared at different temperatures and ammonia flow rates for 4 h under water vapour.

TaON (JCPDS file 01-070-1193) was observed at 900 °C and ammonia flow rate range of 40–50 cm^3/min (Fig. 4). A bright yellow TaON powder has been reported by other researchers previously and has been found to contain slightly more oxygen

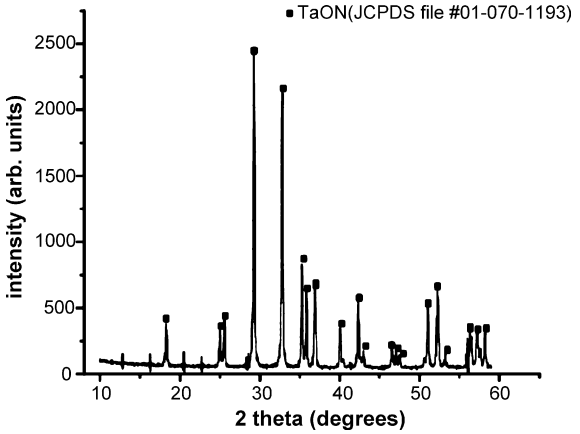

Fig. 4. XRD patterns of TaON obtained by thermal nitridation at 900 °C and 50 cm^3/min ammonia flow rate for 4 h.

Table 1
Experimental analysis results comparison of experimental (ONH analyser) and calculated oxygen and nitrogen contents obtained at 900 °C and an ammonia flow rate of 50 cm^3/min

Nitridation time (min)	Nitrogen (wt%)	Oxygen (wt%)	Formulation
60	3.32 ± 0.12	10.90 ± 0.42	$TaO_{1.44}N_{0.50}$
240	6.77 ± 0.29	7.45 ± 0.03	$TaO_{0.98}N_{1.02}$
360	7.41 ± 0.18	6.81 ± 0.29	$TaO_{0.9}N_{1.12}$
Calculated	6.64	7.58	TaON

Error magnitude is due to the standard deviation.

content than the ''olive green'' phase [5]. This phenomenon was also observed in the present work after partially oxidising the ''olive green'' TaON at 600 °C for 5 min. The reason for such a phenomenon is well-documented in earlier studies [5].

A nitridation temperature of 900 °C and in the ammonia flow rate range of 40–50 cm^3/min was regarded as the most favourable nitriding condition for TaON in the present work (Fig. 3). The change of the nitridation time between 60 and 360 min at 900 °C and a flow rate of 50 cm^3/min results in different oxygen/nitrogen ratios despite the fact that the sample showed only TaON peaks in the XRD pattern. The values obtained at 240 min correspond to the ideal data. Therefore, this nitridation time was used for the preparation of the powders for the sintering experiments.

Particle morphology by SEM reveals a submicron range of TaON particles (Fig. 5). This is clearly confirmed in Fig. 6 below which shows an average particle size of ~2 μm. The surface area of powders was reduced by a factor of ~3× during nitridation as revealed by BET results, a surface area of 2.01 ± 0.02 m^2/g was recorded. This particle growth could be due to amorphous-crystallised phase transition leading to crystallite formation/growth.

TGA under flowing air at 10 °C/min shows that the oxynitride phase starts to oxidise into the oxide phase at ~690 °C (Fig. 7). This reflects the oxynitride–oxide transition temperature in air. A transition temperature of ~630 K has been reported in previous studies [5]. The transformation is

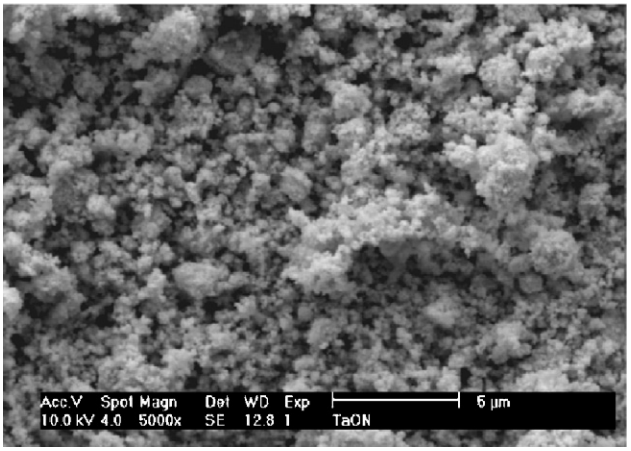

Fig. 5. SEM micrograph of TaON powder obtained by nitridation at 900 °C and NH_3 flow rate of 50 cm^3/min for 4 h under water vapour.

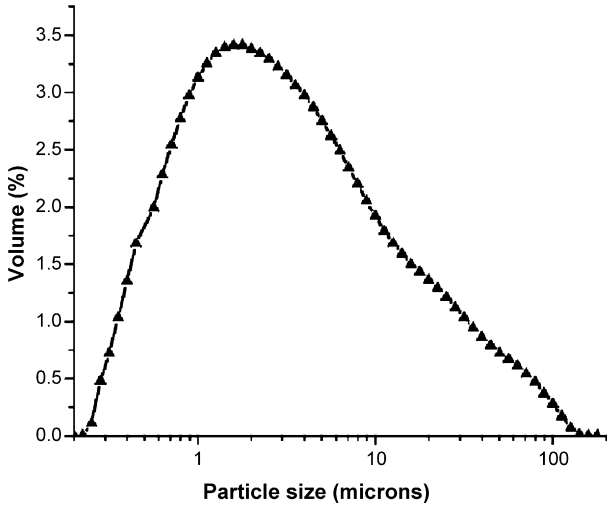

Fig. 6. Particle size distribution of the TaON powder obtained by nitridation at 900 °C and NH_3 flow rate of 50 cm^3/min for 4 h under water vapour.

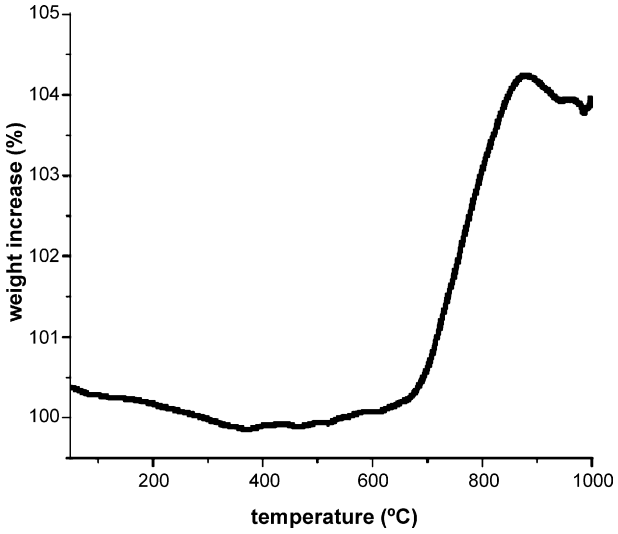

Fig. 7. TGA curve for the thermal decomposition of TaON in air heated at 10 °C/min up to 1000 °C.

associated with a colour change from olive green to white. The theoretical weight gain associated with the stoichiometric oxidation of TaON to Ta_2O_5 is ~4.74% which is quite comparable with a value of 4.38 ± 0.02% obtained clearly showing a complete oxidation of the TaON phase.

3.2. Densification and characterisation of the dense materials

The powders were densified by two different methods, i.e. hot pressing and ultra high pressure sintering. Hot pressing in BN crucibles at temperatures up to 1400 °C and 1 h isothermal sintering time in Ar (99.99%) resulted in porous samples as highlighted in Table 2. Additionally the samples contained some Ta_2O_5 beside the TaON. As a result ultra high pressure solid state sintering has been used to obtain better-densified materials. The densification temperature was varied between 920 and 1200 °C. The different conditions and the properties of the resulting materials are given in Table 2. Some oxidation was observed at 1200 °C, Fig. 8, under ultra high pressure sintering. The polished section of sample 5 is shown in Fig. 9. From the polished section it can be seen that the sample is fully dense

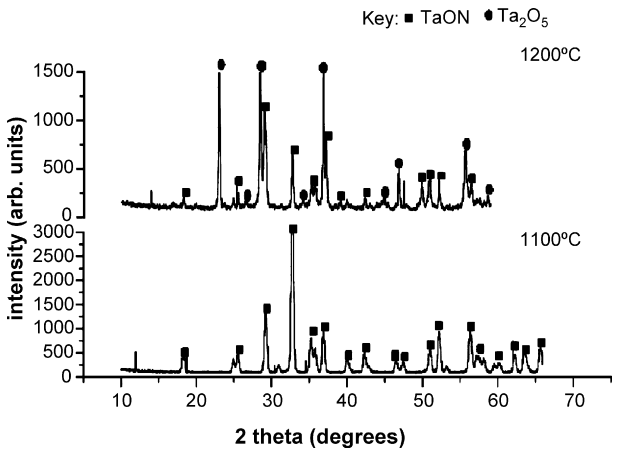

Fig. 8. XRD peaks of the observed phases at 1100 °C and oxidation at 1200 °C during high pressure sintering.

with few large pores remaining. The grain size of the materials was approximately 1.5 μm as derived from examination of fractured surfaces. The phases observed were the monoclinic TaON, i.e. no phase transformation took place during the high

Table 2
Properties of prepared TaON-phases

Sample	Sintering temperature (°C)	Pressure (GPa)	Time (min)	Density (g/cm^3)[a]	Phase purity	Hardness (HV10) (GPa)	Fracture toughness (MPa $m^{1/2}$)
Hot pressed samples							
1	1000	0.05	60	7.28	TaON	–	–
2	1200	0.05	60	6.25	TaON + Ta_2O_5	–	–
3	1400	0.05	60	7.07	Ta_2O_5	–	–
High pressure sintered samples							
4	920	5.5	15	9.74	TaON(m)[b]	16.4 ± 1.1	2.6 ± 0.7
5	1100	3	15	9.54	TaON(m)	16.2 ± 0.5	3.8 ± 1.1
6	1100	3	30	9.53	TaON(m)	17.7 ± 0.5	3.9 ± 0.6
7	1200	3	30	–	TaON + Ta_2O_5	16.9 ± 1.7	2.9 ± 0.4

[a] Density determined by Achimedes' method; theoretical density of TaON: 10 g/cm^3 [15].
[b] Monoclinic phase; error magnitude is due to standard deviation of five different measurements.

Table 3
Comparison of the properties of TaON with ZrO_2–HfO_2-ceramics

Material	Phases	Vickers hardness (HV10) (GPa)	K_{IC} (MPa $m^{1/2}$)	Literature
TaON	Monoclinic	16–17	3–4	This work
Y-TZP	Tetragonal/cubic	12.5	8–12	[17]
PSZ (MgO)	Tetragonal/cubic	12.5	8–10	[17]
CSY	Cubic		2–3	[17]
YTZP (3 mol%)	Tetragonal/cubic	13.6	13.0 ± 0.5	[18]
HfO_2 (7 mol%)	39% tetragonal/cubic/60% monoclinic	14.3	3.8 ± 0.5	[18]

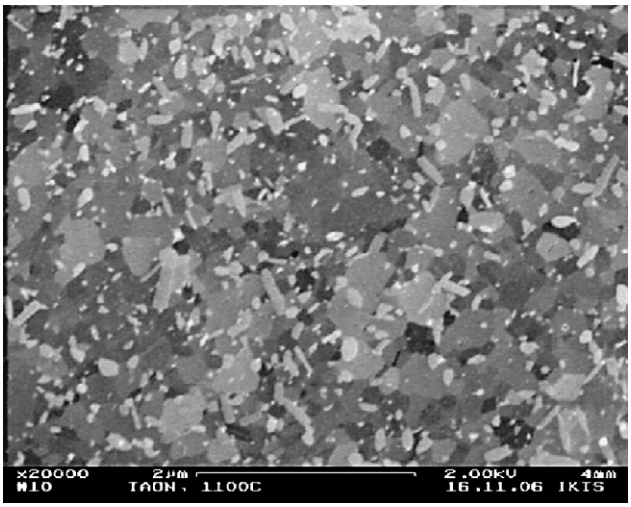

Fig. 9. SEM micrograph showing the etched polished cross-section of sample 6 sintered at 1100 °C and 3 GPa; the white phase contains slightly more nitrogen content.

pressure sintering. An average hardness of ∼16.8 GPa (HV10) and fracture toughness of ∼3.9 MPa $m^{1/2}$ were obtained. Above 1100 °C some Ta_2O_5 phase was observed by both EDX in SEM and X-ray diffraction.

4. Discussion

The densification of TaON materials in the hot press under the same conditions as ZrO_2 ceramics resulted in porous, poorly densified materials. This is on the one hand due to the higher covalence character of the Ta–N bond present in TaON which reduces diffusion during sintering. On the other hand complete oxidation was observed above 1200 °C. The densification of TaON under ultra high pressure (3–5.5 GPa) and temperatures of 920–1100 °C resulted in a slight increase in the hardness with increasing temperature. The hardness values obtained for TaON are higher than those for ZrO_2 or HfO_2 ceramics due to stronger covalent bonding of the nitrogen (Table 3). This is well known from other materials, e.g. Si_3N_4 in comparison to SiO_2. The fracture toughness values are as low as those of fully stabilised ZrO_2 materials since there is no phase transformation toughening. It is expected that TaON would possess a much higher hardness than ZrO_2 from the bulk moduli values (Table 4). However, the low shear modulus value for TaON contributes to its reduced hardness reflecting different shear planes existing in the baddeleyite structure.

Table 4
Comparison of the calculated bulk modulus and the shear modulus of different ZrO_2, HfO_2 and TaON phases

Material	Phases	B (GPa)	G (GPa)	Literature
ZrO_2	Monoclinic	191	–	[1]
ZrO_2	Tetragonal	204	99	[1]
HfO_2	Monoclinic	251	–	[19]
TaON	Monoclinic	280	–	[1]
TaON	Tetragonal	242	70	[1]
ZrO_2	Cotunnite	305	–	[19]
ZrO_2	Cotunnite	254	112	[1]
Diamond	Cubic	442–433	524–544	[1]

5. Conclusion

An X-ray pure TaON was obtained in the presence of water vapour pressure of $\sim 3.1 \times 10^3$ Pa at 900 °C and an ammonia flow rate of 50 cm^3/min. The oxynitride phase was found to be stable in air up to ∼690 °C. The powders were sintered under high pressure and nearly fully densified materials were achieved. No phase transformation was observed and a monoclinic phase similar to that described by Armytage and Fender [16] was observed. An average hardness value of ∼16.8 GPa was observed, which is slightly higher than that of ZrO_2 materials. The fracture toughness is similar to that of fully stabilised ZrO_2.

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