Fabrication of ZrC_xN_y from ZrO_2 via Two-step Carbothermic Reduction-Nitridation

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Abstract

This study examined the processing parameters of a two-step carbothermal reduction-nitridation of ZrO_2 as a UO_2/PuO_2 simulant to fabricate ZrN . Variables studied were the reaction time, reaction temperature and the starting powder composition. Higher temperatures, longer reaction times and higher initial amounts of carbon in the starting material lead to increased nitridation similar to previous work with uranium oxide but that reaction rate decreases with time. SEM and TEM of the reacted powders reveal regions of ZrC with ledges indicative of crystal defects with small particles of ZrN growing on the ZrC bulk material suggesting a reaction that occurs via Zr transport to the reaction site either through mass diffusion or evaporation-condensation of $\text{Zr}_{(g)}$ and with $\text{N}_{2(g)}$ forming the nitride. Annealing experiments on these mixed phases shows formation of a solid solution is rapid compared to the nitridation, where there is no formation of a mixed phase.

Keywords: Nuclear fuel, Inert Matrix Fuel, Carbonitride, Carbothermal reduction, Nitridation

1. Introduction

Carbide and nitride fuels are being considered for application in Generation IV reactors, radioisotope thermoelectric generators (RTG) and accelerator driven systems (ADS) [1–3]. Fuel materials used in the Gas Cooled Fast Reactor (GFR) nuclear power plant will need to withstand higher temperatures (in the region of 1273–1873K) [4], harsher radiation fields due to the hardened neutron spectrum and possess increased thermophysical properties to improve efficiency of heat transfer in the reactor. Non-oxide fuels contain fewer lighter elements per heavy metal, i.e. MN compared to MO_2 (M=metal) giving a higher heavy metal density and therefore a higher fissile density, ideal for use in fast breeder reactors in maintaining a fast neutron spectrum [5]. Recent work has focused on assessing thermophysical properties, such as heat capacity, thermal expansion and thermal conductivity of actinide nitrides, inert matrix candidates and their composites in order to predict the in-pile behaviour of nitride fuels [6].

Zirconium nitride has traditionally been used as hard coatings for power tools [7] but is being considered for use as an inert matrix fuel (IMF) or as advanced fuel particle coating due to its high thermal conductivity, low neutron capture cross section and chemical compatibility with existing fuel cycle technology [8]. Due to this increased interest recent work has focused on assessing thermophysical properties of ZrN and mixed phases of actinide nitrides dispersed in ZrN . However

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difficulty in determining purity and stoichiometry of these materials has lead to much scatter in these properties with the bulk of experimental data being presented for commercially available powders[9–13]. Our work has shown that thermal conductivity of ZrC_xN_y ceramics increases with increasing nitrogen content [14].

While other processing routes such a hydrogenation of metal ingot and nitridation of the metal hydride have been used to fabricate nitrides [15] the carbothermic reduction-nitridation of oxide powders is an economically attractive route for the large scale production of non-oxide fuels due to the large stockpiles of spent mixed oxide fuel (MOX) [16]. Methods of carbothermal reduction-nitridation of oxides generally use similar processing parameters [6, 17], mixing of oxide powder with a carbon source, heat treatment to between 1800-2300K under inert atmosphere and then further heat treatment in a hydrogen-doped nitrogen atmosphere to complete the reaction and remove excess carbon. However, Bardelle and Warin [18] have proposed that the reactive agent during the carbothermic reduction nitridation of UO_2 is HCN rather than N_2 and H_2 separately. The basic mechanism of carbothermic reduction-nitridation is reported [6] to proceed via formation of the carbide from reaction of the oxide with free carbon releasing CO gas. A MC_xN_y phase (where M = metal) is then formed on the surface of the particle and continual removal of carbon via reaction with hydrogen followed by nitrogen diffusion leads to the nitride. The equation for a two-step carbothermic reduction-nitridation is shown below;

Understanding the mechanism of carbothermal reduction-nitridation in these systems will allow it to be exploited for higher purity materials with reduced processing times. In this work a two-step carbothermal reduction-nitridation process was used with the aim of fabricating powders of ZrN and ZrC_xN_y from ZrO_2 with the different processing parameters being assessed to develop an understanding of the underlying mechanism and compare the results to previous work on fabrication of uranium and plutonium nitride assessing the suitability of zirconia as surrogate for this study.

2. Experimental

Powders of monoclinic ZrO_2 ($\geq 99\%$, $\leq 5\mu m$, Sigma Aldrich, Gillingham, UK) and carbon black (≤ 40 nm, ABCR, Karlsruhe, Germany) were mixed to achieve a C/Zr molar ratio of 2.7 and 3.0 (sample names, 1Zr-2.7C and 1Zr-3C respectively). These mixtures were homogenised by ball milling a slurry (in acetone) for 12h using ZrO_2 milling media and dried at 363K. Powders were then subject to a 4h dwell at 2073K (+10K/min) under Ar in a graphite furnace (Fine Ceramics Technologies (FCT) systeme GmbH, Frankenblick, Germany) to produce the corresponding carbides by carbothermal reduction. The resulting powders were then ball milled as in the previous ball milling step. Nitridation of dried powders was carried out for 2-24h at 1800 or 1873K (+35 K/min) under a flowing $H_2(10\%) / N_2$ atmosphere of atmosphere in a tube furnace (50 mm internal diameter and 1200 mm long, flow rate of 0.5 L/min, Lenton, Derbyshire, UK), samples are named ZrCN for zirconium carbide-nitridation and numbered (as labeled in table 1). Samples were stored under in a vacuum desiccator.

For elemental analyses of carbon and nitrogen, oxidation analysis was performed whereby the samples were oxidised at 1173K in air and the resultant CO/CO₂ detected by Infra Red (IR) and N_2 via a thermal conductivity cell (Thermofisher, Loughborough, UK). The chemical analyses are reported as the average of three measurements and the error given as the standard deviation.

FactSage software (ver. 16.2) was used to calculate the reactive gas species at 1873 K and 1 atm. Gaseous species below 10^{-6} mole fraction are omitted.

High resolution transmission electron microscope analysis was performed on the powders using bright field (BF) imaging and selected area electron diffraction (SAED) (HRTEM FX2100, JEOL, Japan), lattice planes were indexed by calculating the d_{hkl} values from the reciprocal of the separation of diffraction spots. Surface characterisation of the as-reacted powders were performed using secondary electron imaging (SEM, Auriga, Zeiss, Germany). Phase analysis was done using X-ray diffraction (XRD) (Pananalytical, The Netherlands) at 40 kV and 40 mA, using Ni-filtered $\text{CuK}\alpha$ radiation.

3. Results and Discussion

3.1. Powder Synthesis

3.1.1. Chemical Compositions

Chemical analyses of carbon and nitrogen using the oxidation technique of the starting ZrC_x powders and the nitridation products are presented in table 1. Table 1 reveals that the two compositions of ZrC had a stoichiometry of $\text{ZrC}_{1.00}$ and $\text{ZrC}_{0.89}$ and increased nitridation was consistently observed for the higher carbon containing stoichiometry. The large error in the carbon content of the $\text{ZrC}_{1.00}$ sample may arise from free carbon remaining in the sample after the carbothermic reduction step and the calculated wt% of C in the sample of 12.4 wt% is slightly higher than the theoretical 11.6 wt% of stoichiometric ZrC. However, even after increased dwell times and reaction temperatures complete removal of carbon was not achieved and the resultant powders from the nitridation experiments were all carbonitrides (table 1). In figures 1 and 2 the combustion analyses of the powders shows the change in C wt% with reaction progression. In both figures it can be seen that wt% carbon decreases with increasing dwell times and temperatures but also that the initial amounts of carbon in the starting samples effect the amount of carbon loss, with higher amounts of initial carbon wt % giving increased rate of carbon loss. This increased rate of loss of carbon may however arise from the presence of free carbon in higher carbon containing sample readily forming hydrocarbons during the initial part of nitridation.[19, 20] Another observation from figures 1 and 2 is that the rate of reaction slows as the reaction progresses, with the decrease in C wt% being higher for 0-8 hour reaction time, than for the 8-24h reaction time. This decrease in rate would be expected, as the reaction proceeds there is less ZrC particle surface area to react with and therefore removal of carbon from the bulk ZrC lattice decreases. The observation of carbon content increasing the rate of reaction has been observed by other authors with regards to the nitridation of UO_2 and has been attributed to the formation of methane/hydrocarbons being in equilibrium with the carbon and hydrogen atmosphere.[19, 20] As either the hydrogen or carbon contents increase the equilibrium shift results in increased formation of methane and therefore higher removal of carbon. Table 2 shows the mole fractions of gaseous species predicted using FactSage, from this it can be seen that HCN is the third highest mole fraction of gas after the H_2 and N_2 atmosphere with the much less stable tautomer of HCN (HNC) and monoatomic hydrogen predicted to form before CH_4 . This higher rate of nitridation seen in samples with higher carbon content would arise from increased HCN formation.

3.1.2. Powder Characterisation

Results of the experiments will be presented in order of increasing levels of nitridation. XRD (figure 3) patterns of powders from the nitridation reaction progression of the $\text{ZrC}_{1.00}$ samples reveals they are crystalline and cubic although each reflection contains two peak maxima corresponding to a composite mixture. The peaks that occur at lower two-theta correspond to

ZrC, which decreases as carbon content decreases with the ZrN peak (peak splitting at higher two-theta) becoming dominant as the reaction proceeds. After prolonged dwell times the ZrN peak increases relative to the ZrC peak. From this it can be seen that increased dwell times and higher dwell temperatures give greater nitridation. Although chemical analyses of the powders indicated there is still carbon present after increased nitridation times (table 1), XRD reveals in the latter stages that no single phase ZrC is present and the carbon may exist in the form of ZrC_xN_y .

SEI micrographs of as-reacted powders revealed different surface characteristics of the powders. Figure 4 reveals the surface microstructure of the as-reacted powders from $\text{ZrC}_{0.67}\text{N}_{0.33}$, showing that the particles have surface ledges which may indicate uniform removal of mass in a specific plane. Bright-field transmission electron microscopy (BF-TEM) of $\text{ZrC}_{0.67}\text{N}_{0.33}$ (figure 5a) reveals a core-rim particle structure, which may arise from Z contrast from different stoichiometries present at the surface, either via destabilisation of ZrC forming ZrC_{1-x} or growth of a ZrC_xN_y layer on the surface of a ZrN particle. The SAED pattern of the particle (figure 5b) reveals a single crystalline pattern of ZrN ([112] zone axis) along with double diffraction streaks, which were observed for another region (figure 5c,d) of the sample, however the SAED pattern in figure 5d indexed well with ZrC ([200] zone axis). Both SAED patterns (figures 5b,d) show double diffraction spots or streaks indicating the presence of two crystals which are in the same orientation and are typical of epitaxy [21]. It can also be seen from the high resolution images (figures 5a,c) that there is registry between the lattice fringes in the core and rim of the particle. The lattice constants for ZrC and ZrN are within 2.6% of each other and both crystals are cubic (Fm $\bar{3}$ m) so distinguishing by electron diffraction is difficult. The satellite streaks seen in figure 5 may be due to diffraction from a second phase of which two scenarios may be possible;

- The streaks in the SAED pattern may also arise from the defects present in this outer layer of ZrC that has reduced C content, which would produce an outer layer of non-stoichiometric ZrC_{1-x} which has been reported to have a slightly larger lattice cell for stoichiometries of $\text{ZrC}_{0.8-0.95}$ [22] and would be consistent with the observation that the crystals are in the same orientation.
- A second phase of ZrC or ZrC_xN_y suggesting the ZrC_xN_y particles grow with ZrC_xN_y phase with higher C content at the surface as carbon diffuses to the reaction layer.

Polycrystalline regions of ZrN were also observed via BF-TEM (indicated by the discontinuous ring pattern in figure 5e,f), although the ZrN reflections in the XRD patterns (figure 3) clearly show a crystalline ZrN phase there may also be regions of the particle where the nitrogen is deposited onto the particle surface in no particular orientation creating polycrystalline regions.

$\text{ZrC}_{0.43}\text{N}_{0.52}$ (nitridation temperature 1800K, dwell time 24h) reacted powders revealed ledges in the particles again with an increased number of spherical particles on the surfaces (figure 6). Formation of ZrN rich separate to the ZrC particles would be consistent with the two monolith phases detected by XRD (figure 3). For the $\text{ZrC}_{0.25}\text{N}_{0.7}$ (nitridation temperature 1800K, 24h) powder almost no ledges are apparent, and the particles look free from any ledge defects with a uniform surface indicating a more complete reaction (figure 7). BF-TEM images of the $\text{ZrC}_{0.3}\text{N}_{0.65}$ powder reveal two regions;

- The first appears to be a ZrC particle revealed by the SAED pattern in figure 8a-d. Figure 8b reveals a ledge similar to those in the SEI micrographs which may correspond to formation of crystal defects. The distance measured between the lattice fringes index well with the (111)_{ZrC} plane and correspond to a lattice parameter of 4.670Å. The lattice parameter calculated from the SAED (figure 8d) of 4.678Å is in agreement with the lattice parameter calculated from the high resolution image and is similar to the literature value of

4.696Å [23], however the decrease may be due to large concentration of vacancies or nitrogen content. Gendre et al.[24] have shown that lattice size of ZrC in mixed ZrC_xO_y phases decreases with decreasing carbon content finding a lattice minimum lattice parameter of 4.680Å.

- The second is a small spherical particle at the surface of bulk, larger particles shown in figure 9a-d which was determined to be ZrN by the SAED pattern. The lattice parameter calculated from the SAED (figure 9d) was 4.624Å, which. The spacings between the lattice fringes in the TEM image (figure 9c) was determined to be 2.666Å which indexed well with the (111)ZrN plane and gives a lattice parameter value of 4.620Å which is in good agreement with the lattice parameter calculated from the SAED pattern. Although the calculated lattice parameters are larger than the ZrN lattice parameter of 4.579Å [25] the decrease compared to other particles this may particle contains higher nitrogen content.

3.1.3. Discussion of Synthesis

Different rates of crystal growth in a given direction can be described due to the preference in minimisation of high energy surfaces (i.e. surfaces with a larger number of interactions) over surfaced with low energy (fewer available interactions), from this it could be assumed that the opposite would apply to crystal destruction, whereby there is a preference to remove mass from a low energy plane instead of a high energy plane. The observation of terrace-ledge-kink mechanism is typical of crystal growth or dissolution.[26] In this mechanism three types of faces are seen; flat, stepped and kinked. For a cubic system, crystals in the flat face have 5 bonds with other crystals, stepped faces have crystals with 4 bonds and kink face crystals have 3 bonds (depicted in figure 10). From this bonding order it can be seen that during dissolution the removal of a crystal at the kinked face will be easier than crystals at the stepped face, with the most difficult to remove being crystal at the flat face, this gives rise to the structures observed in the SEI micrographs of nitrided powders (figure 4). Similar observations of crystal defect formation resulting in ledge formation of particles were made by David et al. [27] with regards to the carbothermic reduction of ZrO_2 to ZrC, whereby the reaction of ZrO_2 with free carbon results in removal of oxygen from the lattice. The resulting ZrO_{2-x} is reduced continually until $\text{Zr}_{(g)}$ forms at the particles surface which then combines with free carbon to nucleate ZrC. This removal of oxygen and zirconium from the particle leads to the formation of crystal defects and ledges in the particles. A similar mechanistic effect could be occurring here, whereby removal of carbon from the lattice via reaction with hydrogen creates substoichiometric ZrC_{1-x} which then reacts further until a metal-rich layer of Zr exists at the particle surface. This surface removal of C and Zr from the particle may also be the reason for the observation of the core-rim structure of the particles corresponding to Z contrast in the BF-TEM images. This contrast difference also accounts for why the layer thickness at the surface of the particle does not increase with reaction time, if indeed they were ZrN layers diffusing into the the ZrC particle. The increase in the number of these spherical particles observed in the SEI micrograph (figure 6) and the BF-TEM images (figure 9a-c) suggest the ZrN particles form at the surface of the larger ZrC particles. This again agrees with observations by David et al. [27] that the nucleation of $\text{Zr}_{(g)}$ and C occurs at a point separate to the particles surface. In the case that a nitrogen-rich Zr phase grows at the surface of the bulk ZrC particles so that two mechanisms of growth may be possible, either evaporation-condensation of $\text{Zr}_{(g)}$ and $\text{HCN}_{(g)}$, or the migration of Zr at the particles interface which then reacts with $\text{HCN}_{(g)}$. Similar observations have been noted with the carbothermal reduction-nitridation of silica where Si_3N_4 nucleates and grows a point separate to the SiO_2 bulk particles and grows from that point to a larger Si_3N_4 particle.[28, 29] This mechanism however, is in contrast to the mechanism of carbothermal reduction-nitridation of UO_2 reported by Mukejee et al. [19] and Bardelle and Warin [18], whereby an initial layer of carbonitride forms at the

surface of UC, which then becomes UN on top of UC with carbon diffusing to the reaction layer being removed by reaction with hydrogen followed by the diffusion of nitrogen into the particle until a UN particle exists.

3.2. Mechanism

An overall proposed mechanism for the reaction is shown in figure 11, the details of the stages of the mechanism are detailed in the following;

3.2.1. Destabilization of ZrC

The crystal defects observed in the ZrC crystal (figure 8b) may result from the removal of carbon leading to formation of ZrC_{1-x} by hydrogen, via equation 3. With the continual removal of carbon, metal-rich regions at the surface of the particle start to form, leading to gaseous $Zr_{(g)}$ (showing in the upper left part of figure 11). The formation of these Zr and C deficient regions is revealed by both the formation of ledges in the ZrC crystal and the contrast fringes at the edges of all particles.

3.2.2. Nucleation of ZrC_xN_y

Small spherical particles that SAED indicates are ZrN or N-rich ZrC_xN_y were observed on the surface of the bulk ZrC particles by TEM and SEM (figures 6 and 9) which may form by the migration of Zr from the ZrC_{1-x} phase or condensation of $Zr_{(g)}$ with $HCN_{(g)}$ (equation 4). The ZrC_xN_y particles then grow uniformly in a direction from the ZrC particle with carbon migrating from the core to the particles surface resulting in a lower carbon ZrC_xN_y phase at the core of the particle until a single ZrN phase exists with a ZrC_xN_y phase at the particles surface (figure 11). This propagating carbonitride phase accounts for the observation of a mixed phase by XRD (figure 3) where there is no definite separation between the ZrC and ZrN peaks. A mixed phase may also occur at the ZrC_{1-x} fringes of the particles where nitrogen could occupy the vacancies.

3.2.3. Growth of Nitrogen Rich ZrC_xN_y Phase

Growth of the ZrC_xN_y particle then propagates by further migration of Zr to the reaction layer and condensation of $HCN_{(g)}$. An external layer is then formed on the ZrC_xN_y particle as carbon diffuses to the reaction layer to form more $HCN_{(g)}$ leading to a carbon rich external layer, and a nitrogen rich core (equation 5) which is consistent with the SAED patterns observed with a minor phase with a increased lattice parameter in epitaxy with the bulk phase (5b and d).

A solid solution formed on annealing in vacuum (figure 12) suggesting that during the reaction the uniformity of carbon removal and nitride growth results in little mixing of carbon and nitrogen during the reaction, however under vacuum the two elements can interchange sites easily due to their similar masses and atomic radii.

4. Conclusion

Mixed phase ZrC_xN_y powders were produced using the established carbothermic reduction and nitridation process. Increasing nitridation temperature and dwell times increased nitrogen content in the powders, however all still contained interstitial carbon (present as ZrC in XRD) even at long dwell times of 24 h. Nitridation of ZrC occurs in two steps, first the destabilisation and removal of carbon in the ZrC particle by reaction with hydrogen leading to the formation of $\text{Zr}_{(g)}$ and $\text{HCN}_{(g)}$ followed by the condensation of these two gaseous species at regions near the surface of the ZrC particle leading to formation of ZrN.

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Figure 1: Change in wt% carbon in samples heated to 1800K

Figure 2: Change in wt% carbon in samples nitrided at 1873K

Figure 3: XRD patterns of nitrided powders compared with literature [23, 25]

Figure 4: SEI image of $\text{ZrC}_{0.67}\text{N}_{0.33}$ powder (sample ZrCN-3, reaction temperature 1800 K, dwell time 8 h)

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Figure 6: SEI image of $\text{ZrC}_{0.43}\text{N}_{0.52}$ powder (sample ZrCN-7, reaction temperature 1800 K, dwell time 24 h)

Figure 7: SEI image of $\text{ZrC}_{0.25}\text{N}_{0.7}$ powder (sample ZrCN-6, reaction temperature 1800 K, dwell time 24 h)

Figure 8: BF-TEM image of ZrC particle in $\text{ZrC}_{0.3}\text{N}_{0.65}$ powder (sample ZrCN-9, reaction temperature 1873 K, dwell time 24 h), a) low magnification of region a, b) high magnification of ledges in region a, c) high magnification of particle in region a, d) SADP of region in c

Figure 9: BF-TEM image of ZrN particle in ZrC_{0.3}N_{0.65} powder (sample ZrCN-9, reaction temperature 1873 K, dwell time 24 h), a) low magnification of region a, b) high magnification of region a, c) high magnification of white box in b, d) SADP of region in c

Figure 10: Types of crystal surfaces, F - flat face, S - stepped face and K - kinked face

Figure 11: Schematic of proposed mechanism of nitridation of ZrC

Figure 12: XRD patterns of $\text{ZrC}_{0.67}\text{N}_{0.33}$ after annealing in vacuum for 1 and 2 h at 1873 K

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Sample	Starting C/Zr mol ratio	Dwell time / h	Dwell temperature / K	Atmosphere	at% C	at% N	Stoichiometry
1Zr-2.7C	2.7	4	2073	Ar	44.42 $\pm$ 1.82	2.42 $\pm$ 0.39	ZrC _{0.89} N _{0.04}
1Zr-3C	3.0	4	2073	Ar	49.76 $\pm$ 6.06	1.99 $\pm$ 0.57	ZrC _{1.00} N _{0.04}
ZrCN-1	3.0	4	1873	10% H ₂ - 90% N ₂	33.54 $\pm$ 0.47	13.76 $\pm$ 1.29	ZrC _{0.68} N _{0.28}
ZrCN-2	3.0	8	1800	10% H ₂ - 90% N ₂	25.15 $\pm$ 0.43	24.20 $\pm$ 0.58	ZrC _{0.50} N _{0.48}
ZrCN-3	2.7	8	1800	10% H ₂ - 90% N ₂	33.50 $\pm$ 0.14	16.30 $\pm$ 0.34	ZrC _{0.67} N _{0.33}
ZrCN-4	3.0	8	1873	10% H ₂ - 90% N ₂	28.52 $\pm$ 0.78	18.00 $\pm$ 0.29	ZrC _{0.57} N _{0.36}
ZrCN-5	2.7	8	1873	10% H ₂ - 90% N ₂	25.03 $\pm$ 0.23	20.72 $\pm$ 0.42	ZrC _{0.5} N _{0.45}
ZrCN-6	3.0	24	1800	10% H ₂ - 90% N ₂	12.09 $\pm$ 0.49	34.86 $\pm$ 0.02	ZrC _{0.25} N _{0.7}
ZrCN-7	2.7	24	1800	10% H ₂ - 90% N ₂	21.25 $\pm$ 0.35	26.23 $\pm$ 0.06	ZrC _{0.43} N _{0.52}
ZrCN-8	3.0	24	1873	10% H ₂ - 90% N ₂	6.04 $\pm$ 0.25	39.23 $\pm$ 0.22	ZrC _{0.12} N _{0.78}
ZrCN-9	2.7	24	1873	10% H ₂ - 90% N ₂	14.81 $\pm$ 0.75	32.26 $\pm$ 0.37	ZrC _{0.3} N _{0.65}

Table 1: Carbon and nitrogen analysis of nitrided powders using different starting compositions, dwell times and dwell temperatures

Species (g)	Mole fraction / 10^{-2}
N ₂	89.311
H ₂	10.501
H-C-N	0.1678
H	0.0120
H-N-C	0.0058
CH ₄	0.0011
C ₂ H ₂	0.0009

Table 2: Mole fractions of gaseous species present during nitridation of ZrC powder at 1873 K under flowing H₂(10%) - N₂ gas calculated using FactSage