Effect of Fructose on Preparation of Nanocrystalline Zirconium Nitride Powder by Internal Gelation Combined with Carbothermic Nitridation

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Abstract. Nanocrystalline zirconium nitride (ZrN) powder was prepared by using internal gelation combined with carbothermic nitridation. As a carbon source, fructose was added in the internal gelation process to facilitate a homogeneous dispersion. Fructose was decomposed and ultrafine carbon was generated in-situ at high temperature. The ultrafine carbon acted as a reducing agent to remove oxygen atoms in carbothermic nitridation process. The effects of fructose on phase composition, morphology, grain size and specific surface area were analysed. The carbothermic nitridation led to a peculiar morphology in the powder particles. The sample with maximum content of ZrN (88.5%) can be obtained when C/Zr = 1.5. And sample with highest specific surface area (237.6 m²/g) can be realized when C/Zr = 2.

1. Introduction

As an advanced ceramic material, zirconium nitride (ZrN) has attracted much attention due to its good physical and chemical properties [1]. It possesses high melting point, high hardness, good corrosion resistance and good chemical compatibility with actinides [2-5]. ZrN has been proposed ascabots [6-8], Josephson junction in electronics [9] and ceramic matrix of inert matrix fuel (IMF) [10-12]. Besides, since ZrN has a structure similar to uranium nitride (UN), so it is often used as a surrogate for fabrication of UN fuel in nuclear reactors [13, 14].

Zirconium nitride powders have been prepared by hydrogenation-nitridation method [15], high energy reactive ball milling [4], microwave plasma method [16], as well as reduction nitridation process with different reducing agents such as carbon [17], aluminium [18], and magnesium [1]. It is noteworthy that carbothermic nitridation process has the simplicity for a large scale production. However, it is difficult to obtain nanocrystalline ZrN powders by this route. ZrN particles with nanocrystalline feature have higher surface area and excellent sintering properties. Hence it is effective in fabricating fully dense material [19].

In this study, carbothermic nitridation process was combined with internal gelation method to prepare nanocrystalline ZrN. Internal gelation method could realize homogeneous dispersion of reactants, and reduce dwell temperature and dwell time in heat treatment [20]. Also this process is dust-free [21]. Furthermore, fructose was selected as reducing agent, which decomposed at high temperature and ultrafine carbon particles were generated in situ. The effects of fructose on heat behaviour, phase composition, morphology, grain size and specific surface area of samples were analysed in detail.
2. Materials and Experimental

Raw materials for internal gelation method include zirconyl nitrate \((\text{ZrO(NO}_3)_2\cdot x\text{H}_2\text{O, 99.5\%}, \text{Aladdin, Shanghai, China})\), urea \((\geq 99.0\%, \text{Sinopharm Chemical Reagent, Beijing, China})\), hexamethylenetetramine \((\text{HMTA, \geq 99.0\%, Yongda Chemical Reagent, Tianjin, China})\), and fructose \((\text{C}_6\text{H}_{12}\text{O}_6, 99\%, \text{Aladdin, Shanghai, China})\).

The internal gelation process started with preparation of solution I to give 1.6 mol/L ZrO\(^2+\) and different amount of fructose in deionized water, and solution II consisting of 3 mol/L HMTA and 2.625 mol/L urea in deionized water. In solution I, the molar ratio of carbon in fructose and zirconium atoms was represented by C/Zr, which was set as 1, 1.5, 2, 2.5 and 2.75. Then 20.0 mL of solution II was added dropwise into 28.7 mL solution I. Zirconium hydroxide gel mixed with fructose formed. The mixture was further heated in a water bath at 80°C for 1 h. Then the gel precursor was washed with deionized water, and dried at 60°C for 12 h in air.

The carbothermic nitridation of gel precursor was carried out under flowing nitrogen\((99.99\%)\) using alumina tube furnace (SENTRO Technologies, USA). Nitrogen was still used during cooling to prevent oxidization. The heating rate and cooling rate were both 10°C/min, and the flowing rate of nitrogen was 100 mL/min.

The gel precursor and fructose were analyzed using a thermo-analyzer (TGA/DSC 3+, METTLER TOLEDO, Switzerland) under nitrogen atmosphere. The phase identification of samples was carried out by X-ray diffraction (XRD, D8 Advance, Bluker, Germany) with Cu K\(\alpha\) radiation (\(\lambda=0.154056\) nm) at 40 kV for the angle (2\(\theta\)) ranging from 10° to 90° and with a step size of 2°/min. The relative contents of different phases in samples were calculated by semi-quantitative analysis based on the HighScore Plus software. The morphology of the samples were observed by scanning electron microscope (SEM, SU8220, Hitachi, Japan) with an energy dispersive spectrometer (EDS). The Brunauer-Emmett-Teller (BET) specific surface area of the powders was measured by using a fully automatic surface area analyzer (Quantachrome, AutosorbIQ Station 1).

3. Results and Discussion

3.1. Thermal analysis of fructose and gel precursor

The chemical formula of fructose is \(\text{C}_6\text{H}_{12}\text{O}_6\). Theoretical carbon content in fructose is 39.9 wt\%. Figure 1(a) shows simultaneous thermogravimetric analysis, differential scanning calorimetric analysis (TGA/DSC) and differential thermal gravity analysis (DTG) for fructose under nitrogen atmosphere from room temperature to 1000°C. It shows the carbonization of fructose in nitrogen atmosphere. A continuous weight loss (~72.8%) occurred from 120°C to 400°C as shown in the TGA curve. Maximum loss rate was around 270°C in the DTG curve. After decomposition of fructose, amorphous carbon generated in situ and the final amount of carbon at high temperature 1000°C is 16.7%, which is lower than the theoretical value. This loss of carbon might be due to that the carbon particles were carried away with gas release in the decomposition process.

Figure 1(b) shows thermal analysis of zirconium hydroxide gel precursor mixed with fructose at nitrogen atmosphere. The TGA curve can be divided into five distinct regions corresponding under temperature ranges from room temperature to 180°C, 180-400°C, 400-850°C, 850-1200°C, and beyond. The first step, from room temperature to 180°C, a weight loss of ~7.3% corresponds to evaporation of absorbed water. The second step (180-400°C) weight loss of ~39.4% involves carbonization of fructose and removal of the other residual organics. And the maximum loss rate is around 208°C in the DTG curve. The third step (400-850°C) relates to the crystallization of zirconia. Two significant weight losses, ~5.4% (850-1200°C) and ~8.7% (1200-1500°C), can be detected in the TGA curve. They reveal a two-step carbothermic nitridation process, corresponding to initial nitridation and further nitridation, respectively. The endothermic peaks around 980°C and 1300°C in the DSC curve are associated with those two steps of carbothermic nitridation process.
3.2. The effect of fructose on the phase composition
Based on the thermal analysis shown in figure 1, 1400°C was selected as a suitable dwell temperature for nitridation. Figure 2(a) shows XRD patterns of samples treated at 1400°C for 5 h under flowing nitrogen. Before XRD characterization, samples were grinded in an agate mortar for 30 min. In figure 2(a), the diffraction peaks around 2theta ~ 33.97°, 39.38°, and 56.81° demonstrated the presence of rock-salt type cubic structure of ZrN (JCPDS file no 00-035-0753). The diffraction peaks of ZrN phase show that fructose was an effective carbon source in carbothermic nitridation process.

The effect of fructose on the phase composition of samples is shown in figure 2(a). The molar ratio of carbon in fructose and zirconium (C/Zr) ranged from 1 to 2.75. From XRD patterns, three phases were found in the sample with C/Zr = 1, i.e., zirconium nitride, zirconium oxynitride ZrO11N2 (JCPDS file no 00-048-1637) and monoclinic zirconia (JCPDS file no 00-037-1484). When C/Zr = 1.5 ~ 2.75, two phases, zirconium nitride and zirconium oxynitride, can be detected in figure 2(a). The relative contents of m-ZrO2, ZrO11N2 and ZrN in samples were calculated by HighScore plus software. The calculated result is shown in figure 2(b). With the increase of C/Zr, the relative content of zirconium nitride increased firstly, then decreased; correspondingly zirconium oxynitride decreased. The highest relative content of zirconium nitride is 88.5wt% when the value of C/Zr is 1.5.

**Figure 1.** TGA/DSC/DTG curves of (a, upper) fructose (b, bottom) gel precursor mixed with fructose under nitrogen atmosphere.

![TGA/DSC/DTG curves](image-url)
Figure 2(b) indicates that the relationship between C/Zr and relative content of ZrN phase in samples was nonlinear. An optimum molar ratio of fructose and zirconium about 1.5 existed at which a maximum content of ZrN was achieved. In carbothermic nitridation process, increasing fructose content (increasing the value of C/Zr in range 1 ~ 1.5) will increase the interface area between zirconia and carbon regions. However, further increasing fructose content (C/Zr > 1.5) will be deleterious to the reduction and nitridation reactions due to the increased solid state diffusion distance of atoms involved in the reactions between those regions.

The effect of fructose on the grain size of ZrN was also investigated. Based on the XRD patterns and Debye-Scherrer formula, the grain size of ZrN was calculated and is shown in figure 3. It indicates that ZrN crystals in samples were nanocrystalline. All the grain sizes were below 50 nm. With the increase of fructose amount, the grain growth of ZrN was impeded.

Figure 2. (a) XRD patterns of samples with different C/Zr treated at 1400°C for 5 h under flowing nitrogen, (b) relative contents of m-ZrO₂, Zr₇O₁₁N₂ and ZrN in samples.

![XRD patterns and relative contents](image1)

**Figure 3.** Grain size of ZrN in samples with different C/Zr.

3.3. The effect of fructose on the morphology

Figure 4 (a ~ e) shows SEM images for the overview of samples with different C/Zr treated at 1400°C for 5 h. It demonstrates all of them are composed of micron sized particles. Furthermore, the surface morphology of the particles is shown in figure 5(b), which is a magnified image of the red circle.
signed in figure 5(a). A peculiar morphology can be revealed that the surface of particles is full of nanocrystallites.

Further EDS analysis is shown in figure 6. Region 1 and 2 represent the nanocrystallite region and the non-nanocrystallite surface region, respectively. Comparing the elements distribution of region 1 and 2 shows higher nitrogen content and lower oxygen content in region 1. A higher oxygen content and a lower nitrogen content are found in region 2. Combining this result with the XRD patterns in figure 2(a) reveals that region 1, the nanocrystallite, is zirconium nitride phase, and region 2 is zirconium oxynitride phase.

![Figure 4](image1.png)  
**Figure 4.** The overview of samples treated at 1400°C for 5 h. (a–e) C/Zr = 1, 1.5, 2, 2.5 and 2.75, respectively.

![Figure 5](image2.png)  
**Figure 5.** (a) SEM image, (b) magnified SEM image of the red circle signed in (a).

Figure 7(a ~ c) are high resolution SEM images of samples with different C/Zr. They show the detailed morphologies of particles. When C/Zr is 1, particles consist of tight arranged grains. No nanocrystallites are found on the surface of the particles. When C/Zr is 1.5, it shows grain growth and partial sintering of nanocrystallites on the particles surface. When C/Zr is greater than 1.5, a homogeneous distribution of nanocrystallites on the particles surface can be observed. Besides, in Figure 7(c ~ e), the size of nanocrystallites decreases with the increase of C/Zr. It is consistent with the calculated grain size of ZrN shown in figure 3. The decreased grain size of nanocrystallites is related to a longer solid state diffusion distance with the increase of fructose in carbothermic nitridation process.
Figure 6. EDS analysis of the sample with fructose as carbon source.

Figure 7. The high resolution SEM images of samples treated at 1400°C for 5 h. (a~e) C/Zr = 1, 1.5, 2, 2.5 and 2.75, respectively.

3.4. The BET specific surface area analysis
Table 1 presents the specific surface area of samples based on BET analysis. It demonstrates the effect of fructose on the specific surface area of samples. The specific surface area of samples increased with the increase in C/Zr from 1 to 2. Further increase in C/Zr from 2 to 2.75, the specific surface area decreased along with increase in fructose. The highest specific surface area is up to 237.6 m²/g when C/Zr is 2 in sample.

After carbothermic nitridation process at high temperature, the products could maintain high surface area in our study. This was due to the peculiar morphology and introduction of fructose. Firstly, the peculiar morphology that ZrN nanocrystallites homogeneously distribute on the surface, greatly enriched the samples surface area. Secondly, fructose not only acted as a carbon source in carbothermic nitridation process but a sacrificial template as well. In the decomposition process of fructose, a large amount of gas-products were released from the gel precursor, which left large amount of pores in solid reactants. Therefore, the samples had a high porosity when fructose was used as a
carbon source. However, the measured surface area decreased at the on further increasing the C/Zr (2.5 and 2.75). In this case, the concentration of zirconia was insufficient to maintain structural integrity at the increased temperature.

| C/Zr | Specific surface area (m²/g) |
|------|-----------------------------|
| 1.00 | 149.1                       |
| 1.50 | 181.9                       |
| 2.00 | 237.6                       |
| 2.50 | 211.9                       |
| 2.75 | 194.1                       |

4. Conclusions
Nanocrystalline zirconium nitride powder was prepared by using internal gelation combined with carbothermic nitridation with fructose as a carbon source for the first time. The highest content of zirconium nitride was obtained at C/Zr = 1.5. The samples had a peculiar morphology that nanocrystalline ZrN homogeneously distributed on particles surface. With increase in C/Zr, the grain size of ZrN decreased. In addition, nitrided samples had high specific surface area and the highest surface area was up to 237.6 m²/g at C/Zr = 2. In future research, the conversion mechanism of carbothermic nitridation process will be further investigated and the purity of nanocrystalline zirconium nitride will be improved.

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