Synthesis of Ultra-High Temperature ZrC Ceramic Powder by Sol-Gel and Spark Plasma Sintering Method

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Abstract. In this work ultra-high temperature zirconium carbide (ZrC) powders were synthesized using sol-gel method combined with Spark plasma sintering (SPS). It can be concluded that SPS sintering for synthesis powder were both fast and efficient. Grain growth of ZrC particles could be also limited due to the fast heating rate. Temperature over 1700 °C will lead to the fast formation of ZrC powder. Pure ZrC powders could be obtained with an grain size of 100-500nm at temperature of 1750 °C for 5min. Due to the fast heating/cooling rate, long heat treatment period is significantly reduced and the grain size could be strongly suppressed.

1. Introduction
The need for ultra-high temperature ceramics(UHTC) that can operate at temperatures efficiently above 2000 °C has driven the development of new compounds consisting of materials with melting points above or around 3000 °C[1]. Zirconium carbide (ZrC) is one of the most attractive transition metal carbides with wide applications for its unique properties, such as high refractory, high hardness, good wear resistance and chemical stability[2]. Much effort has been made to produce nano-sized carbides by the carbothermal reduction of powder mixtures. Various mixtures, including C-Zr [3-5], C-ZrH2[6], and C-ZrO2[7], have exhibited large particles, contamination, and severe agglomeration due to the high temperatures used in their formation[8]. However, for the strong covalent bonding, ZrC sintering usually requires high applied load and temperature and or the use of sintering aids. Hence, finding a synthesis route for high purity ZrC nanopowder is desirable.

A variety of synthesis routes have been developed to prepare ZrC powders. Among these methods, the sol-gel process is proved to be an effective way to obtain ultra-fine ZrC powders for the high intimacy and low synthesis temperature[9-11]. However, during the traditional heat treatment, higher temperature and longer reaction time were required to further complete the reactions by a progressive removing of oxygen impurity. Unfortunately, it also induced undesirable grain size increase. It has been reported that the grain growth of zirconia (ZrO2) usually occur especially at the temperature higher than 1300 °C, at which the carbothermal reaction is just initiated. Thus, suppressing the ZrO2 growth is of primary importance in the preparation of ZrC nanopowders[13-15].

Spark plasma sintering (SPS) has been demonstrated to prepare nanocrystalline ceramics with a minimal grain growth[16]. Due to the fast heating/cooling rate, long heat treatment period is significantly reduced and the grain growth is strongly suppressed[12, 17].
2. Experimental procedures

The powder-gel process is shown schematically in Figure 1. A block co-polymer surfactant P123 (Sigma-Aldrich) was dissolved in 99.7% ethanol. Zirconium n-propoxide (ZNP) (Sigma-Aldrich) 70 wt% in 1-propanol was chelated with acetylacetone (AcAc). The composition ratio of P123:EtOH:AcAc:ZNP in the sol was 0.05:40:1, yielding a brown sol. Furfuryl alcohol (C₅H₆O₂) (FA) (Sigma-Aldrich) was added and turning the sol an intense yellow. After stirring for 48h, the gel turned dark brown. Oven drying is used to evaporate the ethanol then calcination in tube furnace at 550°C to decompose the PFA and ZNP into carbon and ZrO₂. Other paragraphs are indented (BodytextIndented style).

![Flow chart for the synthesis of zirconium-containing organic precursor.](image)

For SPS (Model 1050, Sumitomo Coal Mining Co. Ltd., Kanagawa, Japan), 3 g precursors were directly placed into the graphite crucible without being pressed. The graphite crucible was specially designed for powder synthesis, and the surface of that was coated with BN to prevent the reactions between the die and reactants. The reduction was conducted in vacuum atmosphere at a heating rate of 100oC/min and the temperature was monitored by an optical pyrometer focusing on the surface of graphite crucible.

Thermogravimetric analysis (TGA) of the zirconia/carbon ratio used a Perkin Elmer DTA/TG 6300 analyser in air at a heating rate of 3°C/min. A FEI Nova nanoSEM was used for scanning electron microscopy. All the microscopes were equipped with EDS for qualitative chemical analysis. XRD was performed using a Bruker D8 Advance, using CuKa radiation (40 kV, 40 mA). Quantitative Rietveld analysis was performed using Bruker TOPAS® V4.2. Scanning over 2θ range 10o-90o used a step size of 0.005°.

3. Results and discussion

In sol-gel method, Zr(OPr)₄ was combined with a mixture of solvents to form a sol/gel. Generally, metal alkoxides are well known to react spontaneously with water and to form precipitates resulting from successive hydrolysis. Xie et al. [13] reported that Zr(OPr)₄ could be modified by acac as bridging and chelating ligands to form zirconium acetylacetone by the substitution of acac for OPr groups. Here, AcAc was used as both chemical modifier and solvent to control Zr(OPr)₄ hydrolysis, and the general reactions occurring during the precursor preparation are shown as follows.
However, FA monomers are constantly lost during wet chemistry and certainly evaporated. Catalyst hydrochloric acid played an important role during sol-gel process for carbon maintaining since it will allow furfuryl (FA) to be hooked together in long chains and formed the PFA. However, PFA pyrolysis to carbon depends on the amount of acid (HCl) catalyst added[16]. Different ratio of HCl was added to the sol solution and after calcination, only carbon and ZrO₂ left, as seen in Figure 2(a) and (b).

Figure 3 shows the TGA analysis of different acid adding into sol-gel solution after calcination in tube furnace for 2h. Flowing air was applied through the TGA process to consume the C. It can be concluded that carbon started to react with oxygen at the temperature of 400°C and ended at 550°C. After calculation, the mole ratio of ZrO₂ and C is 1:3.4 that is sufficient for future carbon reduction. The reactions is as follows: ZrO₂+3C → ZrC+2CO.
Figure 4 shows the FT-IR spectrum of the as-prepared zirconium-containing organic precursor. The peaks at 876 cm\(^{-1}\) is assigned to the characteristic absorption bands of Zr-O-Zr, indicating that there are Zr-O-Zr segments in the polymer chain of the precursor. The peak at 1022 cm\(^{-1}\) corresponds to the C-O stretching vibration. The peaks at 1392 cm\(^{-1}\), 2841 cm\(^{-1}\) and 2914 cm\(^{-1}\) are attributed to the C-H absorption bands and the peaks at 1495 cm\(^{-1}\) and 1603 cm\(^{-1}\) represent the peaks of the C=C stretching vibration of the benzene ring, which indicates that the FA reacted with hydrochloric acid and formed long chain of PFA. the strong absorption at 3415 cm\(^{-1}\) was due to O-H, and the absorption at 1529 was due to C=C in the acetylacetonate ligand[15].

Figure 5. XRD patterns of the pyrolysis products obtained by SPS heat treatment from 1400°C to 1800°C for 5min with Zr/C molar ratio 1:10.
Figure 5 shows the XRD patterns of the pyrolysis products of the ZrC precursor in SPS furnace at various temperatures. As can be seen from XRD profiles, the product prepared at 1400°C is only composed of tetragonal phase zirconia and monoclinic phase zirconia. When the heat treatment temperature increasing to 1500°C, the diffraction peaks of ZrC are detected. From 1500°C to 1700°C, diffraction peaks of hexagonal ZrC and ZrO₂ are both observed in the XRD patterns, which suggest that the energy is not high enough for carbon-thermal reduction, and it could be better to extend the soaking time. When the temperature increased to 1750°C, only the ZrC diffraction peaks could be found, no impurity phase is detected, indicating that ZrO₂ has been converted to ZrC totally, which suggests that the soluble organic precursor can be completely converted to ZrC by the pyrolysis reaction. At the temperature of 1800°C, the phase remained the same with the temperature of 1750°C.

Figure 6 shows the grain growth and the formation of ZrC under different temperature sintering in SPS. At 1500°C, some ZrC and ZrO₂ grain start to appear from the matrix, as seen from the Fig 6a. From the XRD analysis, the ZrO₂ was the main peaks surrounded with C. However, when kept at 1600°C for 5 min, the matrix break for ashes. The fast formation period of ZrC appeared at the temperature of 1700°C. When keep at 1700°C for 5 min, the growth of crystal structure was very similar to steps, as seen from Fig 6c. According to layer growth theory, the edge and angle of crystals have a better chance to accept the particles.[18] Thus nanoparticles would aggregate and forming a two-dimensional nucleus on the surface followed with the spreading of the two-dimensional nucleus across the surface. At the same time, other layers start to grow. When the soaking time finished, the layers and slopes were reserved. From 1700°C to 1750°C, the grain size increased a lot. Moreover, the Crystal growth stripe also exist as shown in Figure 6d. When increase the soaking temperature to 1800°C for 5 min, the average grain sizes increased to 500nm, and some boundary are not clearly to identified. The grain growth takes place at the late stage of sintering and grain size rapidly increases[14]. Due to the fast heating/cooling rate, long heat treatment period is significantly reduced and the grain size is around 100-500nm that could be strongly suppressed.

Figure 6. Formation and grain growth of ZrC under different temperature in SPS for 5 min (a) 1500°C (b) 1600°C (c) 1700°C (d) 1750°C (e) 1800°C.
4. Conclusions
(1) ZrC submicron-sized powders were successfully synthesized by a novel method of combining the sol-gel method and rapid synthesis using spark plasma sintering (SPS). The ratio of Zr:C required for achieving this purity was 1:10.

(2) The fast heating rate in SPS leads to a strong retarding effect on the growth of ZrO₂ particles. Grain growth of ZrC particles could be also limited due to the fast heating rate.

(3) Temperature over 1700 °C will lead to the fast formation of ZrC and a significantly grain growth. Pure ZrC powders could be obtained with an average grain size of 100–500nm at a temperature of 1750°C for 5min.

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