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Effect of pH on Production Process and Characteristics of Zirconium Carbide Nano Particles Synthesized by Sol-Gel Method

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Abstract Zirconium carbide nanoparticles were synthesized by a sol–gel method. Zirconium n-Propoxide and sucrose were used as sources of zirconium and carbon, respectively. The influence of pH value of solution on the properties of the resultant powder was investigated. The reactions were substantially completed at a relatively low temperature (1400°C). X-ray diffraction and scanning electron microscopy were used to study crystal structure and morphology of the synthesized powder. XRD analysis showed that at the highest pH, only ZrC phase could be observed. Results also show that pH has a strong effect on the particles size range of ZrC powder so that at pH 4.2, 5.2 and 6.2, the size range of 130–190, 90–150 and 50–100 nm were obtained, respectively. It was also found that pH variation had no effect on the morphology of the sphere-shaped particles.

Keywords: *zirconium carbide, sol–gel, pH value, particle size*

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1. Introduction

Zirconium carbide (ZrC) has recently attracted researchers' attention towards itself. Due to having a mixture of covalent, ionic and metallic bounding, this specific carbide exhibits several various salient characteristics [1]. ZrC is one of the known hard compounds with a micro-hardness of 2600 kg mm^{-2} [2]. Moreover, a high melting point (3550°C), high resistance to corrosion, appropriate chemical stability, resistance to thermal shock, and thermal and electrical conductivity are among the important properties of ZrC [2,3]. These properties together with some other remarkable ones have increased interest in the application of ZrC in some industries such as nuclear industry [4], composite reinforcement [5], cutting tools [6], surgical implants [7] and electronic devices [8].

Several methods for the preparation of ZrC powders have been reported, such as self-propagating high temperature [9], carbothermal reduction of ZrO_2 at elevated temperatures [10] and chemical vapor deposition [11]. Most of these methods, in particular carbothermal reduction method, require high reaction temperature for ZrC formation, typically, the range of 1800–2200°C with the held time of several hours [6]. Such a high reaction temperature and the relatively large-size particles reacting in solid-state phase lead to the formation of metal carbide products with large-size particles. Therefore, supplementary processes such as hot pressing are essential for producing bulk parts with high relative densities. Recent studies have shown ZrC powders can be synthesized at lower temperature by using precursors that are prepared by solution-based processing methods [12,13,14]. Sol–gel processing is the most commonly used chemical method to produce nano-sized particles in liquid state phase. It is a simple reaction that does not require exotic materials, catalysts or expensive equipment. The studies reported so far have mostly concentrated on producing ZrC powders at different temperature also on determining the properties of the obtained powders. The effect of pH on the properties of ZrC powders has not been discussed in detail, however.

Saks et al. [15] prepared ZrC powders using zirconium n-butoxide and polyhyclric alcohol as sources of zirconium and carbon, respectively. Yan et al. [16] synthesized ZrC powders using zirconium oxychloride as source of zirconium and phenolic resin as the carbon source. These studies suggest although increasing the temperature leads to increasing the purity and decreasing the oxygen contents of the structure, it, however, leads to increasing the crystallites size of zirconium carbide [15–17]. In the present study, we investigated the preparation of ultra-fine ZrC powder by sol-gel method. We also examined the effect of pH variation on the properties of the synthesized ZrC powder.

2. Experimental Procedure

The starting chemicals were zirconium n-propoxide $Zr(OPr)_4$ (70 wt% in 1-propanol, Sigma) and sucrose (99.5 wt%, Sigma) that were used as sources of zirconium and carbon, respectively. Acetic acid (99.8 wt%, Sigma) was

used as chemical modifier of zirconium n-propoxide. Ammonium hydroxide solution (28 wt%, Sigma) was also utilized as pH regulator. Based on the stoichiometric ratio, sucrose was initially dissolved in acetic acid kept at 80°C. Then, zirconium propoxide was added under continuous stirring and formation of sol began immediately. The pH value of the primary sol was 3.2. Then, ammonium hydroxide solution was added during stirring in order to adjust pH of the initial sols to 4.2, 5.2, 6.2 and 7.2. The sols were then stirred under similar conditions (temperature 40°C & stirring speed 200rpm). After, a brown solution was obtained and gelling began. The formed gel was dried to powder at 120°C for three hours. The dried powder was then placed in a tube furnace to undergo the pyrolysis and carbothermal reduction. The pyrolysis was performed with heating rate of 10°C/min, at 700°C under flowing argon atmosphere for 25 minutes. The powder was increasingly heated between 700 and 1400°C at a rate of 20°C/min. The sample was then kept at 1400°C for 150 minutes to undergo carbothermal reduction. Nano-Particle zirconium carbide was then obtained. The ZrC formation was monitored by simultaneous thermal gravimetric analysis and differential Scanning Calorimetry (Netzsch STA 409 PC). Crystallite phases were recorded and identified using X-ray diffraction (XRD, Philips, Cukα). Moreover, crystallites average size (d) was estimated by means of Scherrer Eq. (1):

$$d = 0.9\lambda / \beta.\cos\theta \quad (1)$$

where λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) and θ is the Bragg angle. The present study also used scanning electron microscopy (SEM, TESCAN VEGA2) to determine the sample microstructure.

3. Results and Discussion

Figure 1 shows the simultaneous TGA/DSC curves of the sample at pH 3.2. A weight loss of 10% is observed at approximately 100°C, likely assigned to the loss of absorbed water. An exothermic peak at approximately 550°C is caused by the crystallization of zirconia from amorphous phase to tetragonal phase. There is another exothermic peak centered at 600–700°C, attributed to the reversed tetragonal to monoclinic phase transition of the zirconia. The main stage of the diagram (Figure 1), however, presents the endothermic peak observed at 1300-1400°C. This can be attributed to the carbothermal reduction reaction between the existing zirconia and carbon, and the resultant zirconium carbide phase.

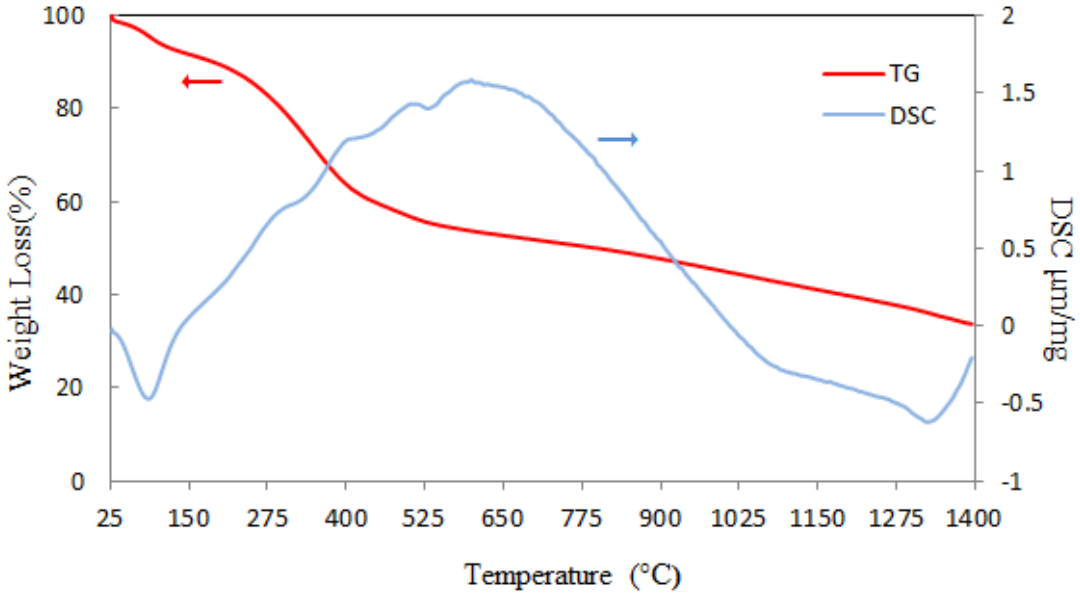

Figure 1. Simultaneous TGA/DSC curves of the sample at pH 3.2

During the sol–gel reaction, sucrose is completely dissolved in the solution and the final gel takes a high degree of homogeneity. After heat treatment of the gel, sucrose is decomposed into atoms of carbon which are then diffused into zirconia. Then, at carbothermal reduction temperature, zirconia could be carburized by carbon to produce ZrC. The reduction temperature required for ZrC synthesis in solid-state precursors is reported to be 1800°C and above [10]. However, as Figure 1 illustrates, the reduction temperature used for the present sample shows a significant decrease (below 1400°C). When compared with temperatures reported by different studies on solid- states, the present temperature decrease not only limits the particle growth but also considerably decreases energy consumption. The advantage of using a gel instead of a physical mixture of the solid compounds is the high intimacy at molecular or colloidal scale. The shorter diffusion distance helps to decrease the heat treatment (dwell temperature and duration) resulting in smaller particles. Carbothermal reduction reaction is given in Eq. (2):

$$ZrO_2(s) + 3C \rightarrow ZrC(s) + 2CO(g) \quad (2)$$

The findings show that at pH 7.2 and above, there are no visible changes in the sol after 4 hours. Under the above-mentioned condition (40°C), it seems that the production of gel is practically impossible at this pH. Table 1 presents the time required for stirring the initial sol up to the formation of the gel under exactly the same temperature and stirring speed.

Table 1. Stirring time of sols for the production of the gel

Sample	pH	Stirring time of Sols(min)
A	3.2	20
B	4.2	55
C	5.2	87
D	6.2	115

As illustrated in Table 1, the time of polymerization or gel formation increases over increasing pH. Increasing the stirring process time ends up with a relatively homogeneous sol and prevents the non-uniformity of the gel. According to Eq. 2, pyrolysis is necessary for carbothermal reduction reaction. This was investigated during the heat treatment of the sample (pH 3.2) at 700°C for 25 minutes under flowing argon atmosphere in a tube furnace. The XRD results of this sample are illustrated in Figure 2.

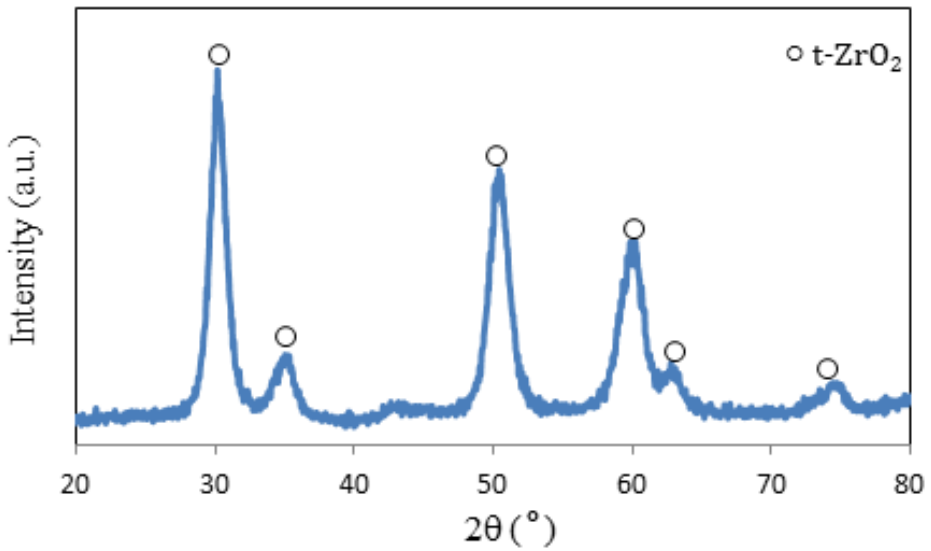

Figure 2. X-ray diffraction patterns of the precursor obtained after heat treatment at 700°C for 25 min

Zirconia phase is the only observable phase in XRD patterns. Since the obtained carbon is amorphous, it cannot be observed in XRD patterns. The result of the scherrer Equation confirmed that Zirconia Crystallites size was 14 nm. Fine-scale mixing of the reactants helps in reducing the carbothermal reduction temperature to produce ZrC. In other words, the sol–gel method ends up with not only uniform and homogenous particles but also the size of its reactant particles is relatively smaller than that of the particles produced by means of other solid-state methods. As mentioned before, in order to perform carbothermal reduction reaction and synthesize the desired powder, the heat treatment was adjusted to 1400°C. Figure 3 indicates X-ray diffraction patterns of the samples.

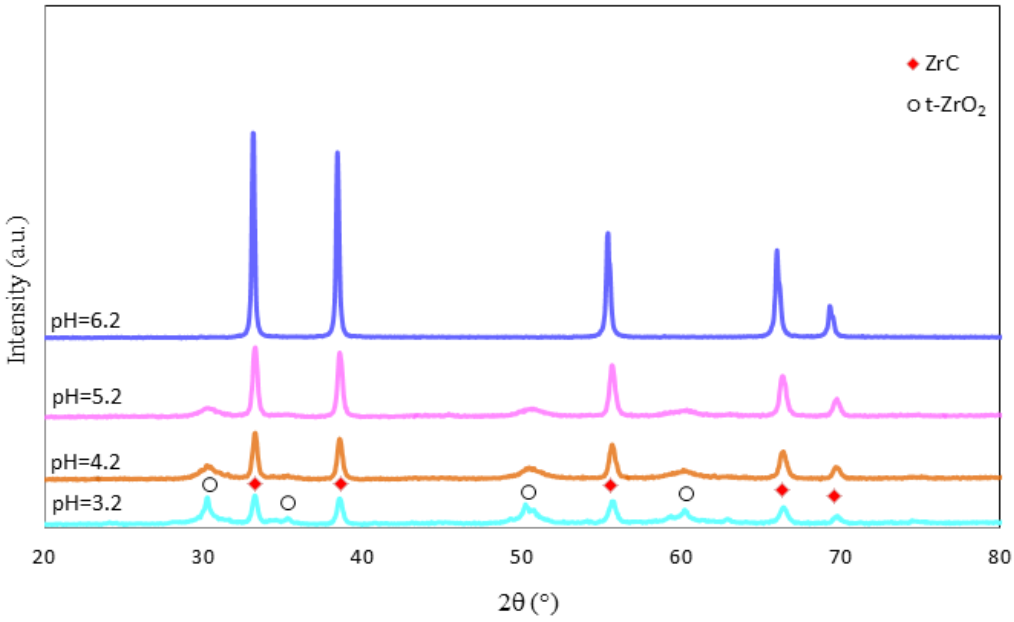

Figure 3. X-ray diffraction patterns of ZrC nanoparticles at different pH values

Figure 3 shows that with the rise of pH, the intensity of Zirconia peaks gradually decreases but the intensity of Ziconium carbide peaks increases. Consequently, only the zirconium carbide phase can be seen at the highest pH. This indicates that the carbothermal reduction process is substantially completed, indicating that ZrO_2 has been converted to ZrC.

SEM images of the synthesized powders and their size range in accordance with pH variation are illustrated in Figure 4 and Table 2.

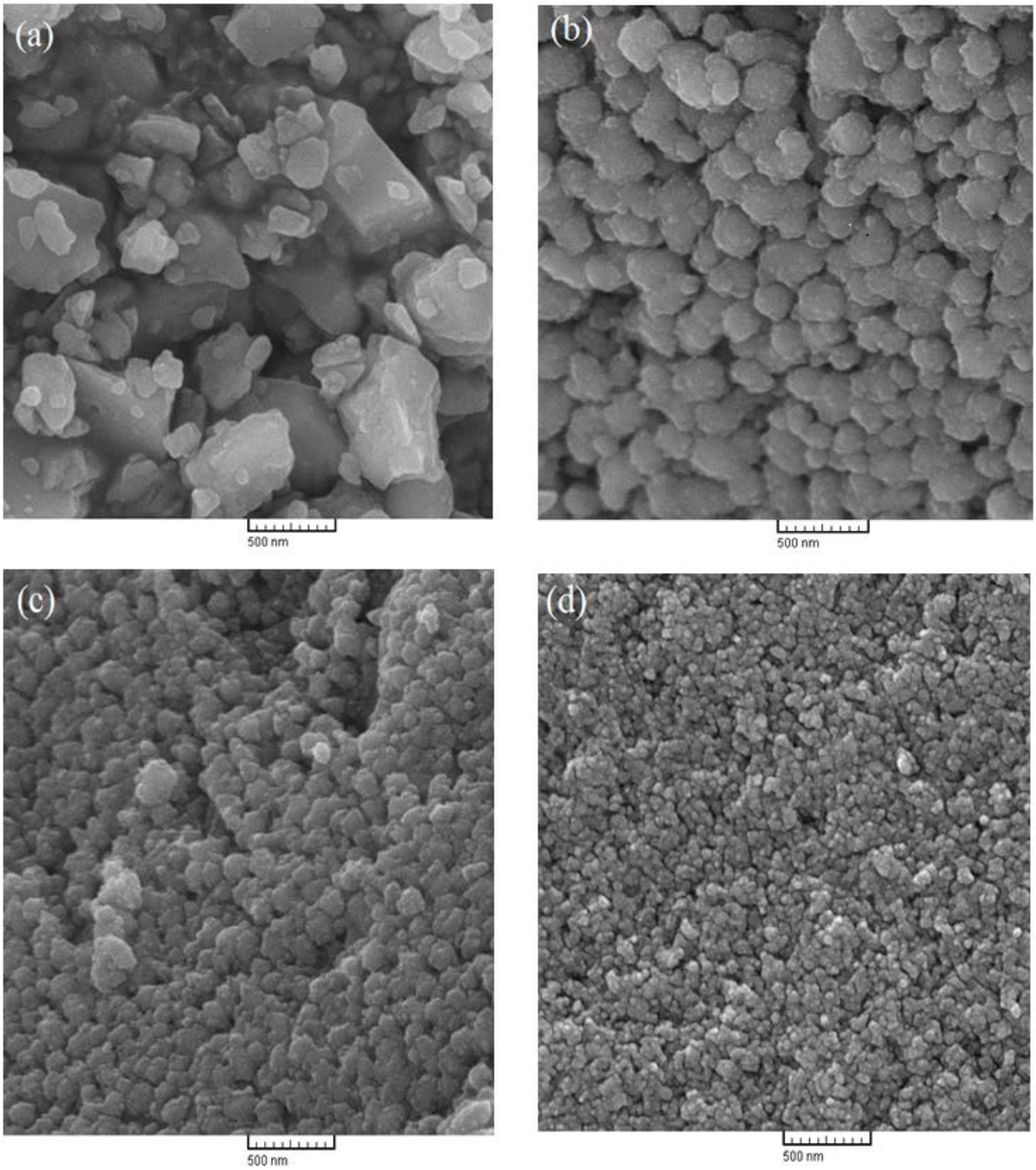

Figure 4. SEM images of the synthesized powder at different pH values. (Samples A, B, C and D at pH 3.2, 4.2, 5.2 and 6.2, respectively)

Table 2. The range of particles size at different pH values

Sample	pH	Range of particle size (nm)
A	3.2	less than 650
B	4.2	130-190
C	5.2	90-150
D	6.2	50-100

The SEM images and pH values reported in Table 2 reveal that pH rising has a significant effect on the reduction of the sizes of ZrC particles so that the smallest particles ranging from 50 to 100 nm are obtained at the highest pH. With respect to increasing the pH from 3.2 to 4.2, 5.2 and 6.2, the particles size ranged from 650 (and below) to 130–190 to 90–150 and 50–100 nm. When compared with the ZrC particles prepared by Yan and his associates [16] and Dolle and his colleagues [17], a noticeable difference is observed in terms of the average particles size.

It should be mentioned that SEM images were examined via Microstructure Image Processing software. The results show that the sample with the lowest pH contains particles that are larger than all. This sample quickly changes from sol to gel, resulting in less homogeneity of the gel. As pH increases, the polymerization process is done at a slower speed, and therefore, the gel becomes more homogeneous. Thus, the particles uniformly join together. This would facilitate both the diffusion of the atoms and the subsequent carbothermal reduction reaction. Therefore, as the reaction time decreases, the diffusion speed increases and this causes the reactants to react, before being influenced by temperature that, in turn, influences their growth. Consequently, the size range of the particles decreases as illustrated by the SEM pictures. Furthermore, the present SEM images illustrate sphere- shape particles, and this is important evidence in support of the insignificant effect of pH on morphology of the particles.

4. Conclusion

Pure, nano-sized ZrC was successfully synthesized by a sol-gel method using Zirconium n-propoxide and sucrose as the starting materials. The obtained carbon and zirconia are minimum in size, and homogeneous and uniform. Therefore, the carbothermal reduction temperature using this method is much lower than that of the initial solid-state raw materials. PH rising ends up with higher purity of the composition also plays an important role in decreasing the particles size of the obtained powder. When followed by homogeneity and uniformity of the gel, pH rising can speed up the carbothermal reduction and enhance its efficiency. The SEM results indicate that the obtained powder at pH 6.2 has the smallest particles size with a range of less than 100 nm. Furthermore, the SEM images indicate that pH variation has no significant influence on the morphology of the particles and the majority of the particles are rather spherical.

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