



Synthesizing of zirconium nitride powders by dynamic thermochemical method

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Abstract

In this study, zirconium nitride (ZrN) powders were prepared using zirconium oxide (ZrO₂) and carbon black via the dynamic thermochemical method, called the dynamic carbothermal reduction and nitridation (DCRN) method. The effects of process temperatures on phase transformation and produced powder morphologies in a dynamic system under flowing nitrogen atmosphere were investigated by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. For this purpose, the various test parameters were investigated, such as reaction temperatures (1400, 1450, 1500 °C), reaction time (1, 2, 3 h) and rotation rates (2, 4, 6 rpm). The results show that ZrN powders of sub-micron size can be obtained at 1500 °C for 1 h and 4 rpm by the dynamic thermochemical method.

Keywords: zirconium nitride, powder synthesis, dynamic thermochemical method, structural characterization

I. Introduction

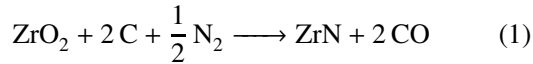
Metal nitrides, a form of non-oxide ceramics, are technologically important engineering materials with good thermal, optical, electrical and mechanical properties. The most popular nitride ceramics include titanium nitride (TiN), zirconium nitride (ZrN), boron nitride (BN) and aluminium nitride (AlN) [1]. Coatings based on zirconium, titanium and chromium nitrides have been used as protective coatings against corrosion and wear because they have low friction coefficient, high chemical stability and high melting point [2]. Zirconium nitride is a synthetic material that is not found in nature, but has a strong bond formed by combining Zr with N. Zirconium nitride structure has high covalent bond characteristics and a NaCl-type cubic crystal structure with a lattice parameter of $a = 0.4586$ nm [3,4]. Zirconium nitride is a promising ultra-high-temperature ceramic material owing to its high mechanical strength, electrical conductivity and chemical stability [5]. It is a technologically important refractory material due to many excellent properties such as high melting point

(≥ 2980 °C), high hardness (2800 HV), high chemical resistance and corrosion resistance, good electrical conductivity ($\sim 200 \times 10^4 \Omega^{-1} \cdot \text{m}^{-1}$), excellent thermal properties, non-toxicity and golden colour [6,7]. Because of these features, ZrN is generally used in medical devices, industrial parts (especially drills), automotive and aerospace components and areas requiring high wear and corrosion resistance. ZrN has also been recommended as a primer for rockets and airplanes [8–10].

ZrN powders are usually prepared by various methods such as direct nitriding of zirconium, reaction of zirconium tetrachloride and ammonia [11], reduction-nitridation process [4,6,12], microwave plasma synthesis [1], mechanical alloying [13], benzene thermal method [14] and self-propagating high-temperature synthesis [15]. Direct nitriding is process in which zirconium metal particles are exposed to nitrogen or ammonia atmosphere at about 1200 °C [3]. Mechanical alloying is method for producing desirable powders in a long time with continuous plastic deformation, fracture and cold welding processes in an inert atmosphere [13]. Carbothermal reduction and nitriding is a thermochemical method that uses oxide-based raw materials and carbon as reductant in a nitrogen atmosphere for short periods at high temperatures. With this method, different

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powders, such as Si_3N_4 [16], Sialon [17, 18], AlN [19] and $\text{NbB}_2\text{-NbC}$ [20], were produced. The reaction of ZrN production by carbothermal reduction and nitriding method is given below:



The conversion of ZrO_2 to ZrN by reduction and nitriding method starts at temperature between 1200 and 1700 °C [4,6,12,21]. Yin *et al.* [4] investigated behaviour of powder mixture prepared with ZrO_2 , Al and CaCO_3 at different reaction temperatures (1400–1700 °C) by the reduction and nitriding method. It was reported that amount of the formed ZrN increases with increasing temperature and then this value decreases. Li *et al.* [21] synthesized ZrN fibres by a high temperature carbothermal reduction and nitridation process with $\text{ZrCl}_2 \cdot 8\text{H}_2\text{O}$ and $(\text{C}_6\text{H}_9\text{NO})_n$ as a raw material mixture at 1600 °C for 5 h in a nitrogen atmosphere.

The aim of this study is to produce high purity ZrN particles from ZrO_2 powder at temperature lower than 1600–1700 °C and short processing time by the dynamic carbothermal reduction-nitridation (DCRN) method as a simple and economical method. In this dynamic thermochemical method, which is a modification of the carbothermal reduction method, the powders are rotated inside a reactor during the reaction, thereby providing a reduction of the reaction time or temperature with the rotation of the powder. In this study, the parameters of ZrN powder production were investigated by the dynamic thermochemical method and the optimum conditions were determined.

II. Experimental

ZrO_2 powder (Sigma-Aldrich, 99%), carbon black (Körfez Petrokimya, 99.9%) and N_2 gas (ARTOK, 99.9%) were used as the reactants. ZrN synthesis from ZrO_2 and C by the dynamic thermochemical (DCRN) method was performed by the reaction described with Eq. 1. The powder mixture was prepared by mixing ZrO_2 with appropriate amount of carbon black (C : ZrO_2 = 2 : 1). Since the aim was to achieve complete conver-

sion without any residual carbon in the structure, carbon was added in the stoichiometric ratio. The dry powder mixture was prepared in a polypropylene container with the zirconia balls. Granulation was carried out in a container with the help of a binder (5 vol.% glycerol-alcohol solution) and the resulting granules were sieved through 1–3 mm mash. The granulation process was carried out to keep the powders together and to prevent powder loss from the reactor.

The prepared granules were put into a graphite reactor in an atmosphere-controlled horizontal-type rotary furnace capable of heating the material up to 1600 °C for the dynamic thermochemical method. The powder mixture was charged into a cylindrical reactor made of graphite with holes on both ends for as to allow gas flow. For the DCRN process, a high temperature horizontal-type atmosphere-controlled furnace (Protherm, max. 1600 °C) was used using a 60 mm outer diameter RCA alumina tube. The furnace was modified so that alumina tube was rotated with the help of a 3 V DC servo motor and gear system. The synthesis was carried out at different reaction temperatures, different reaction times and different reactor rotation speeds (2–6 rpm) while varying the flow rates of nitrogen gas. The schematic representation of the dynamic thermochemical process is given in Fig. 1. The N_2 flow rate of 60 l/h was established after the furnace reached 1000 °C. After the completed heating process, the furnace was cool down from maximal to room temperature. When the temperature reached 1000 °C, the N_2 gas flow was reduced to 3 l/h and held at this level down to room temperature. In addition, the rotation of the furnace tube was stopped at 1000 °C to prevent wear on the graphite reactor. The resulting product (granules) was lightly ground in the agate mortar. Then, the powdered products were characterized by various methods.

Microstructure, size and morphology of the synthesized ZrN powders were characterized by scanning electron microscopy (SEM, JEOL 6060 LV). Energy dispersion spectroscopy (EDS) was used for the elemental analysis. The formed phases were determined by X-ray diffraction (XRD) analysis (Rigaku Ultima). The synthesized powders were analysed using field emission

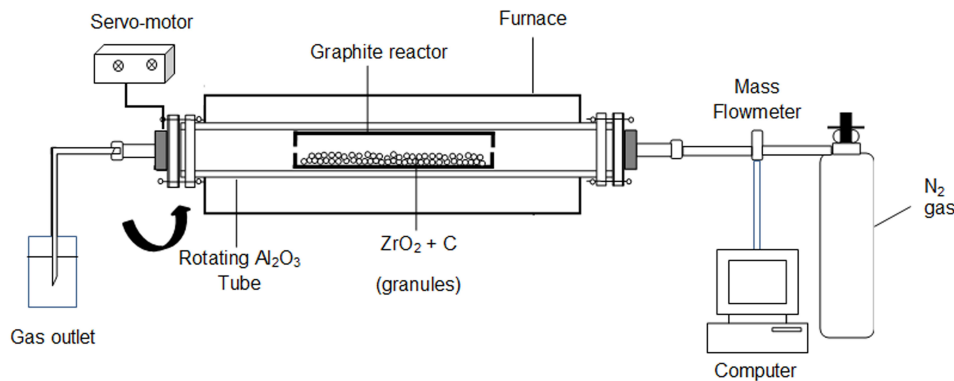


Figure 1. Schematic diagram of experimental process

scanning electron microscope (FESEM). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed on a thermoanalyzer (TA Instruments SDT Q600) in N₂ atmosphere with a heating rate of 5 °C/min. Also, FactSage 7.0 software was used for determination of process parameters.

III. Results and discussion

In this study, the conversion of ZrO₂ powder, which was used as a starting material to produce ZrN advanced technological ceramics by the dynamic thermochemical method, was investigated. XRD and SEM analyses were applied to raw materials and the results are presented in Fig. 2. According to XRD analysis of the ZrO₂ raw material, all of the peaks belong to Baddeleyite phase with card number 01-074-1200. It can be also seen from SEM image (Fig. 2) that the zirconia powder has very small particle size.

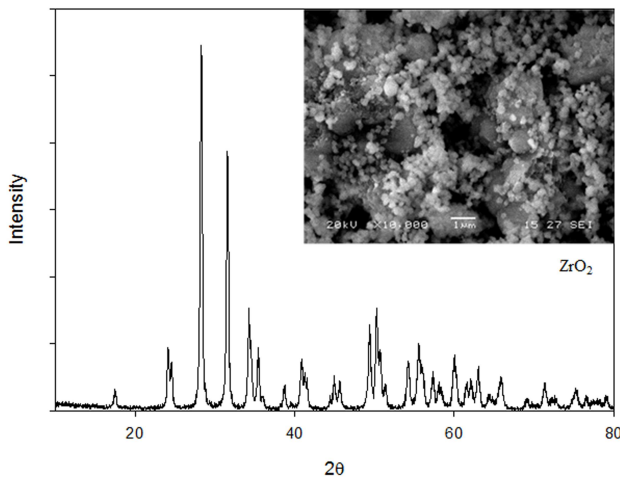


Figure 2. XRD and SEM analysis of ZrO₂ powder

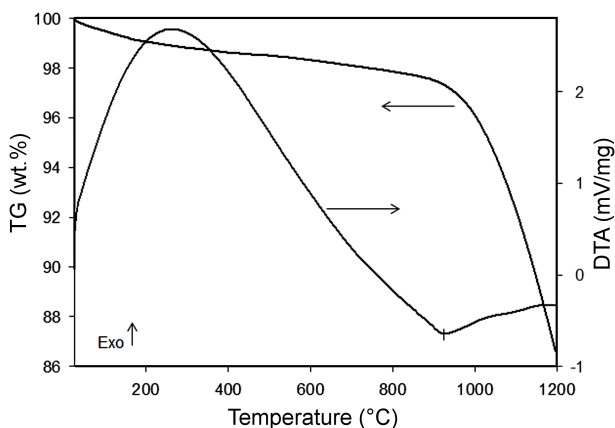


Figure 3. DTA and TG curves of ZrO₂ + C powder mixture

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the ZrO₂ + C mixture was performed before the DCRN process. The analysis was carried out under N₂-atmosphere to determine the onset temperature for the reduction reaction (Fig. 3). Ac-

cordingly, the beginning of weight loss in the TG curve and subsequent endothermic peak in DTA analysis at around 920 °C indicate that the reduction process starts at about 850 °C. Here, the exothermic peak indicating the nitriding reaction expected to occur at higher temperature could not be seen.

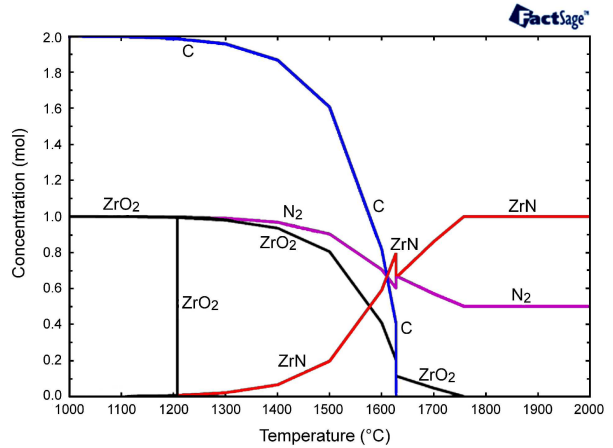


Figure 4. Composition-temperature graph for 1 mol ZrO₂ + 2 mol C and 1 mol N₂ at 1 atm pressure

Analysis of possible and desired synthesis reaction of ZrN from ZrO₂ performed by the FactSage software is shown in Fig. 4. According to the graph, it can be observed that the formation of ZrN starts at approximately 1100 °C. At the same time, the amount of ZrO₂ starts to decrease at this temperature and the amount of C in the system decreases during the reaction. The complete transformation of ZrO₂ and formation of ZrN happen at approximately 1750 °C. The DTA-TG analysis (Fig. 3) indicates the beginning of reduction reaction, but the nitriding temperature could not be determined. Thus, thanks to FactSage software (Fig. 4), the approximate nitriding temperature range (1100–1750 °C) was determined. Therefore, the amount of N₂ gas in the reactor was increased when the furnace temperature reached 1000 °C during the DCRN process.

The granules obtained from the ZrO₂ + C mixture powders before and after the reaction are shown in Fig. 5. As it can be seen, the black granules before the reaction turned into the coloured granules of ZrN (brown) after the reaction. However, there is no great change in the shape and dimensions of the granules during the pro-

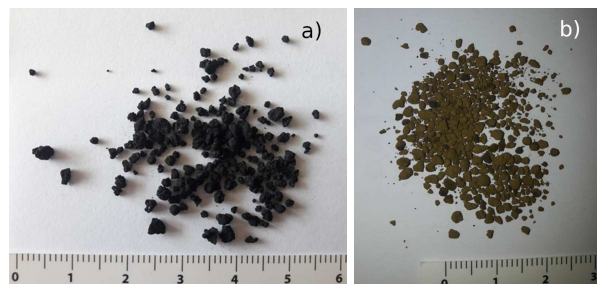


Figure 5. Images of the granules: a) before (ZrO₂ + C) and b) after (ZrN) the process

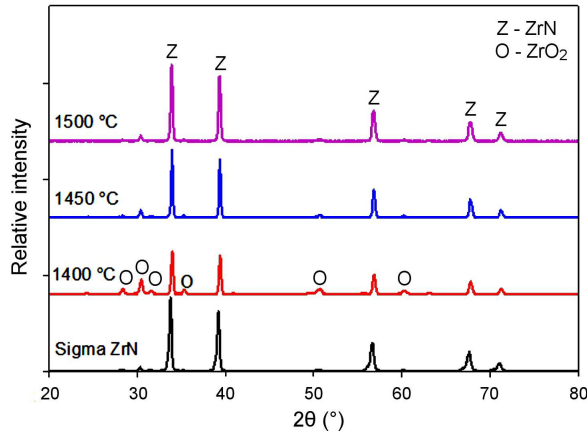


Figure 6. XRD patterns of obtained powders by the DCRN process at different temperatures for 1 h

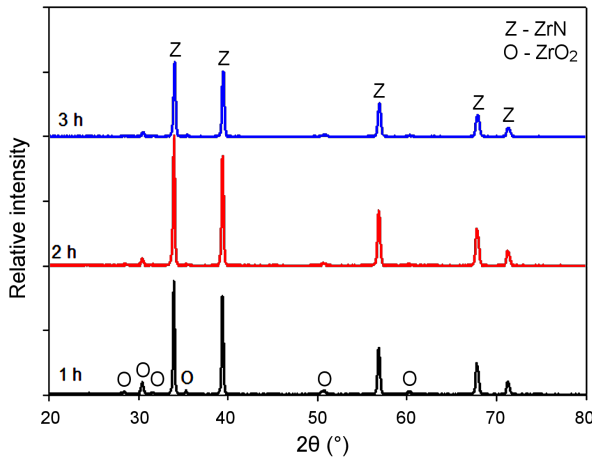


Figure 7. XRD patterns of obtained powders by the DCRN process at 1450 °C for different times

cess. After production, the granules were lightly ground in the agate mortar and a powder product was obtained.

Figure 6 shows XRD patterns of the ZrN powders prepared by dynamic thermochemical process at different temperatures for 1 h and at a constant rotation rate (4 rpm) and the commercial ZrN. In this study, ZrN conversion started at 1400 °C. Considering the DTA-TG analyses, FactSage software results, our similar powder (TiN , Si_3N_4) production studies and literature data [22,23], this temperature was determined as the initial temperature. As it can be seen from XRD analyses, the amount of ZrO_2 decreased with increasing temperature. Therefore, the increase in temperature positively affected the production of ZrN as the amount of unconverted oxide is the lowest and the ZrN peak intensities are the highest at 1500 °C. Also, it could be noted that this result is similar to that for the commercial product (Sigma ZrN). It has also been observed that higher temperatures are not required since the commercial powder-like product with dynamic thermochemical process can be obtained at 1500 °C. Thus, the ZrN powder was obtained at lower temperature compared to both the literature and the FactSage software simulation.

XRD patterns of the powders synthesized by the dynamic thermochemical process for different times (1, 2 and 3 h) at 1450 °C and at a constant rotation rate (4 rpm) are given in Fig. 7. Here, the aim was to examine the possibility to produce ZrN powder at lower temperature by using a long time. According to the XRD analysis, the increase in time caused a decrease in the unconverted ZrO_2 phase. Thus, it was confirmed that the processing time is a very effective parameter which enables ZrN production at temperature as low as 1450 °C. However, since it would be advantageous to produce powder with small particle size, a short time at 1500 °C was selected as optimal processing condition.

XRD patterns of the powders synthesized by the dynamic thermochemical process at 1500 °C for 1 h and different rotation rates (2, 4 and 6 rpm) were shown in Fig. 8. It can be seen that more unconverted oxide phase was observed at 2 rpm and its amount decreases with increasing rotation speed. This is because the increase in rotation speed of the tube caused the granules to come into more contact with N_2 gas and the nitriding process was easier. According to the XRD results, the powders obtained with rotation rates of 4 and 6 rpm are similar, confirming that the optimal rotation rate is 4 rpm.

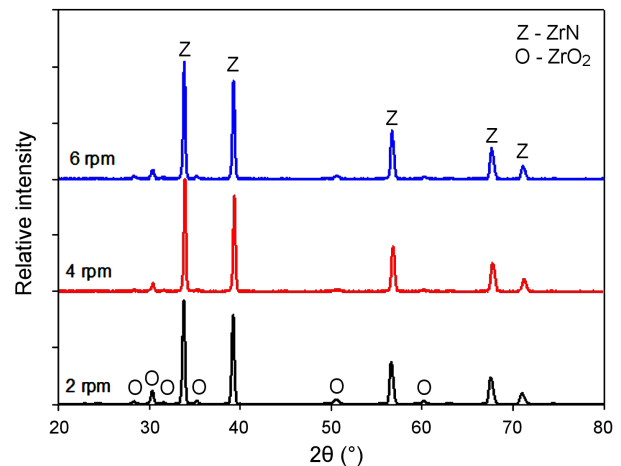


Figure 8. XRD patterns of obtained powders by the DCRN process using different rotation rates at 1500 °C for 1 h

SEM images of the powders synthesized by the dynamic thermochemical process at different temperatures (1400, 1450 and 1500 °C) for 1 h and the commercial ZrN powder are given in Fig. 9. The microstructures are characterised with sub-micron grain size and a regular morphology. In addition, the grain growth was observed with increasing temperature as expected. It is also seen that the powder produced at 1500 °C, which is the best one according to XRD analysis (Fig. 6), has a very fine grain size (Fig. 9c). It is even finer and a more homogeneous compared to the commercial ZrN (Fig. 9d). It has been reported in the literature that ZrN powders with different shapes, such as sub-micron ZrN powders with spherical [4] or fibre-structured ZrN powder [23], can be obtained by using reduction and nitriding method.

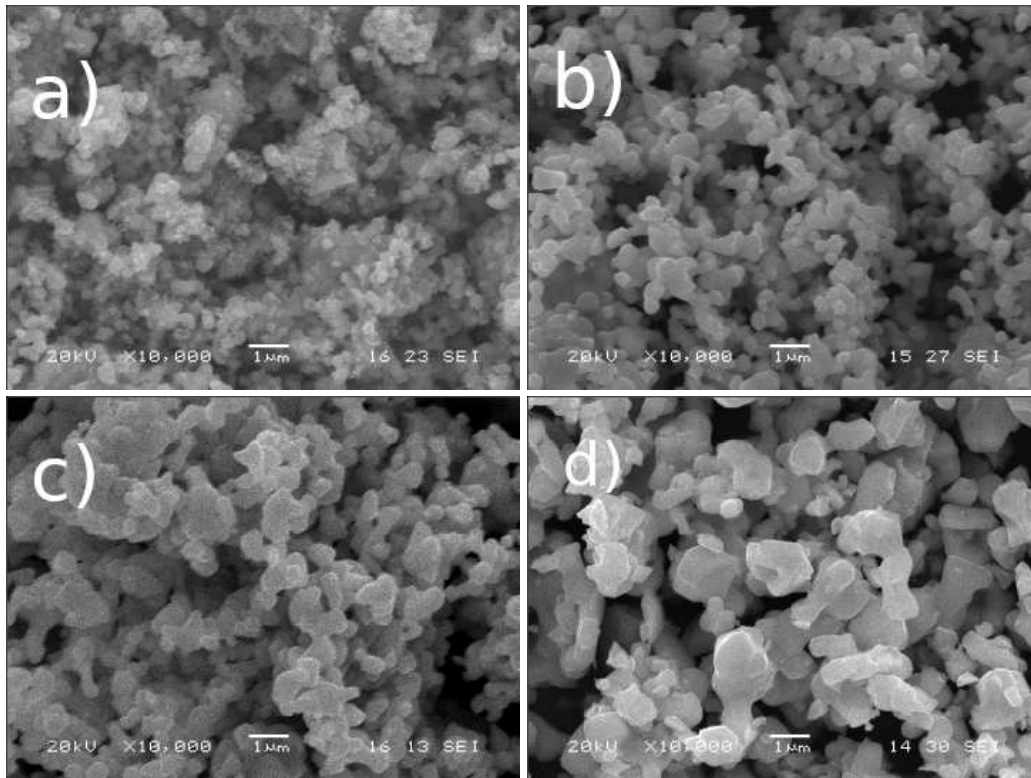


Figure 9. SEM images of obtained powders by the DCRN process at different temperatures for 1 h: a) 1400 °C, b) 1450 °C, c) 1500 °C and d) Sigma ZrN

In this study, the ZrN powder with very small size and close to spherical morphology was obtained economically and in a very short time.

The SEM micrographs of the powders synthesized by the dynamic thermochemical process at 1450 °C for different reaction times (1, 2 and 3 h) are shown in Fig. 10. In general, the produced powders have a sub-micron grain size and a homogeneous structure. As shown, the increase in reaction time did not cause grain growth; this can be considered to be a great advantage for the dynamic thermochemical process. During the process, grain growth did not occur due to the rotational movement of the granules inside the graphite reactor at constant temperature (1450 °C). It is also seen that the grain size is much smaller than for the commercial ZrN (Fig. 9d) despite the increasing time (3 h).

FESEM images (Fig. 11) are used to examine the effect of rotation rates on the powder microstructure. According to the XRD analysis (Fig. 8) the amount of ox-

ide in the powder produced at a rotation rate of 2 rpm is higher than in other samples. It can be seen (Fig. 11) that the powder produced at a rotation rate of 6 rpm has a slightly smaller grain size. In addition, SEM image of the powder produced by the CRN method (static system) is given in Fig. 11a, confirming that the particle size of the particles produced without the rotational movement (0 rpm) have irregular shape and are much larger than that produced by the dynamic system.

The kinetic effect of the granules during the process enabled nucleation to occur more rapidly than expected. In this case, the occurrence of faster reaction ensures that the conversion is completed at low temperature and the particle size is quite small. Considering these images with XRD analysis, the product produced at a rotation rate of 4 rpm at 1500 °C for 1 h by the dynamic thermochemical process gives the best results. It is seen that this microstructure (rotation rate of 4 rpm) has a sub-micron size and moreover it has a grain size of 100–

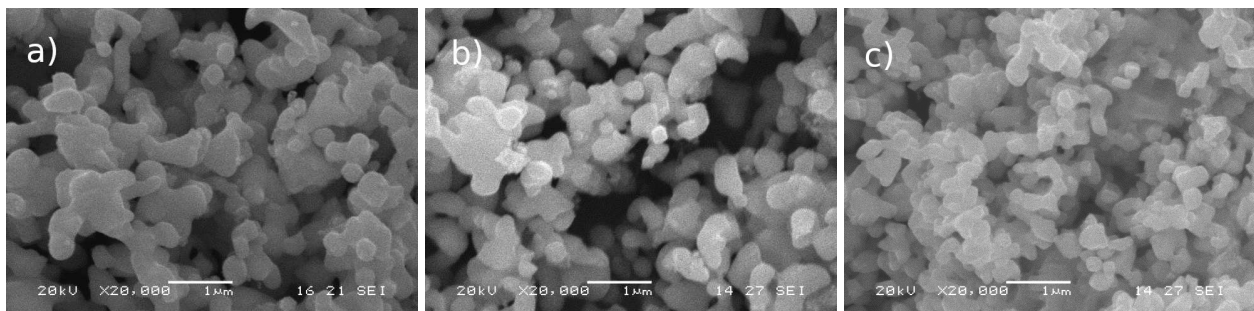


Figure 10. SEM images of obtained powders by the DCRN process at 1450 °C for different times: a) 1 h, b) 2 h and c) 3 h

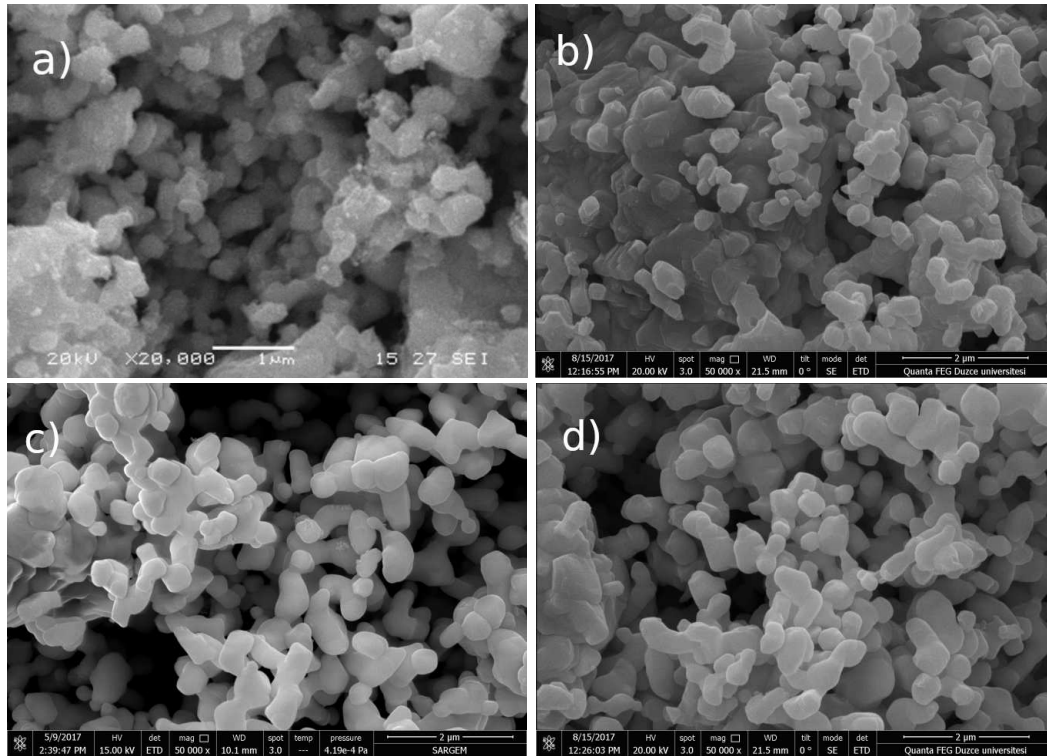


Figure 11. FESEM and SEM images of obtained powders by the DCRN process using different rotation rates at 1500 °C for 1 h: a) 0, b) 2, c) 4 and d) 6 rpm

400 nm. It can also be said that the microstructure is homogeneous, equiaxed and the grain morphology is similar. Thus, within the parameters tested, the conditions (1500 °C - 1 h - 4 rpm) in which ZrN can be synthesized with the desired properties at low temperature and in short time were determined as optimum.

The EDS analysis of ZrN powder produced by the dynamic thermochemical process at 1500 °C for 1 h in 4 rpm rotation rate is given in Fig. 12. According to the results of this analysis, zirconium, nitrogen and oxygen elements were determined. The powder produced by the dynamic thermochemical process has 1.8% oxygen by weight, while the commercial ZrN has 3% oxygen as per EDS analysis. Therefore, the lower oxygen content of the powder produced by the DCRN process can be considered to be an advantage. As the result of experimental studies, powder production at lower temperature

or time was achieved due to the rotational movement of the tube. This effect also occurred during the production of similar powders (TiN powder) by the same dynamic thermochemical process [22], and economical production of powders was achieved. The dynamic thermochemical method is a very economical and energy-saving method because it produces the product in a short time (1 h). In addition, this process has been found to be a very good method for the production of powder with good properties and fine grain size in addition to other advantages.

IV. Conclusions

In this study, fine grained ZrN powders were successfully synthesized by a dynamic thermochemical process using ZrO₂ and carbon black mixed in a stoichiometric ratio. The optimum temperature and time for the full conversion of ZrO₂ to ZrN were determined to be 1500 °C and 1 h. The best result was obtained at a reactor rotation speed of 4 rpm. Thus, ZrN powder having a grain size of about 100–400 nm was produced. The produced powders have a homogeneous morphology with equiaxed very small grains compared with commercial ZrN powder.

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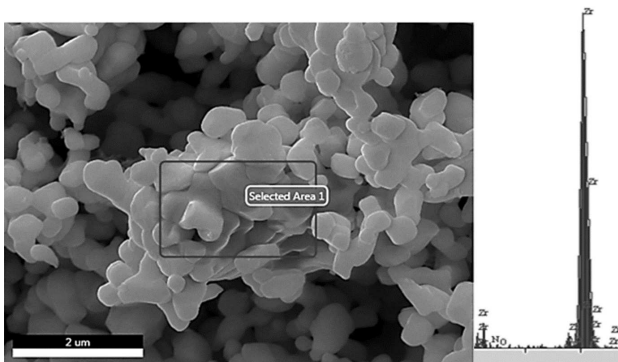


Figure 12. EDS analysis of the obtained powder by the DCRN process at 1500 °C for 1 h and 4 rpm

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