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Preparation of ZrC by self-propagating high-temperature synthesis

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Abstract

ZrC fine powder has been prepared by self-propagating high-temperature synthesis (SHS) based on exothermic reduction reaction of ZrO_2–C–Mg. The combustion temperature observed was 1979 K. The effects of Mg content and particle size on the combustion temperature and chemical composition of the product were investigated. The reducing agent Mg plays an important role on the purity of ZrC powder obtained by SHS process. Post-heat treatment was applied to decrease the oxygen content of the final product further.

Keywords: ZrC; SHS; Combustion temperature; Heat treatment

1. Introduction

Zirconium carbide (ZrC), combining the characteristic properties of metal and ceramic due to a mixture of ionic, covalent and metallic bonding [1], is one of the important high-temperature structure materials. ZrC exhibits various unique properties, such as high melting point (3550 °C), high hardness (25 GP), high corrosion and wear resistance, high electrical conductivity [2], which make it a promising candidate for applications as cutting tools, wear resistant components and crucibles in the mechanical industry [3]; electrical field emitter tips and arrays, especially nuclear reactor core material due to its low neutron cross-section and good irradiation—resistance [4]. Several methods for the preparation of ZrC powders have been reported, such as carbothermal reduction of ZrO_2 at elevated temperature [5], sol–gel process [6], low-temperature synthesis by cyclic reaction of Mg in ZrO_2–Mg–CH_4 [7], mechanical alloying [8] and self-propagating high-temperature synthesis (SHS) technique [9]. SHS is a promising method for the synthesis of materials in virtue of its relative simplicity of process and equipment, as well as efficiency in energy and time, which has found applications in preparing intermetallic compounds and advanced high-temperature materials, particularly carbides, silicides, nitrides and borides [10,11].

In this work, zirconia, carbon black and reducing agent Mg were used for the synthesis of ZrC via the reaction as shown in Eq. (1).

$$ZrO_2 + C + 2Mg = ZrC + 2MgO \quad (1)$$

In the process of combustion synthesis, the reductive degree of oxides has a direct influence on the phase compositions of the synthesized products and thus reducing agent Mg plays an important role in the synthesis of ZrC powder.

In this paper, the effect of Mg content on the combustion process and the purity of products has been investigated; the influence of the particle size of Mg was studied. In order to improve the purity of ZrC powder, post-heat treatment was applied and a proper process route was suggested.

2. Experiment

ZrO_2 powder (purity 99%, monoclinic phase, 15 nm), Carbon black (purity 99.9%, nanoscale) and Mg powder (purity 98.5%, 74, 154 μm) were used as reactants for the synthesis. After being prepared with certain ratio, the reactants were mixed in planetary ball-miller for 5 h, using ZrO_2 balls with diameter of 5 mm as mixing medium. The mixture was dried at 60 °C for 24 h and compacted to form a cylindrical sample under a pressure ranged from 3 to 10 MPa. The sample was ignited by tungsten filament placed close to the top of the sample and was pyrolyzed in the furnace under continuous flow

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of argon gas [12]. The combustion temperature was measured by W5-Re26 thermocouples, which were pre-located in a small hole in close vicinity to the center of the compact. The products were treated by acid-washing method to remove the MgO, and then pure ZrC powder was obtained. The post-heat treatment was applied to increase the purity of the product.

The phase analysis of the product was carried out by X-ray diffractometry (XRD, Ultima, Rigaku, Japan). Morphology of the powders was examined by scanning electron microscope (SEM, Hitachi S-3400N) and high-resolution field-emission SEM (FESEM, Hitachi S-4800). The transmission electron microscope (TEM, H-600 STEM/EDX PV9100) for the acid-washed powder was carried out by putting the ultrasonically dispersed powders on a carbon-coated copper grid. The particle size distribution of sample was determined by a particle size analyzer (ZetaPALs). Oxygen analyzer (Leco TC600) was used to detect oxygen content of the product.

3. Results and discussion

Fig. 1 shows the effect of temperature on the Gibbs energy of possible reaction. It is noted that the Gibbs energy of reaction (a), (b) and (c) are lower than zero in the range of temperature investigated and indicate these reactions could react spontaneously. Thus the process of the SHS reaction of Eq. (1) includes two steps:

$$ZrO_2 + 2Mg = Zr + 2MgO \quad (2)$$

$$Zr + C = ZrC \quad (3)$$

The SHS process is highly exothermic and the entire reaction occurs in a short period of time (few seconds). During the reaction, the sample reaches the highest temperature theoretically, which is called adiabatic temperature (T_{ad}) and can be calculated [13]. The T_{ad} of the reaction of Eq. (1) is 2235 K, according to the theoretical calculation.

The T_{ad} of the combustion reaction of ZrO_2–C–Mg system is much higher than the melting point (923 K) and boiling point (1378 K) of metal Mg. In the process of combustion synthesis,

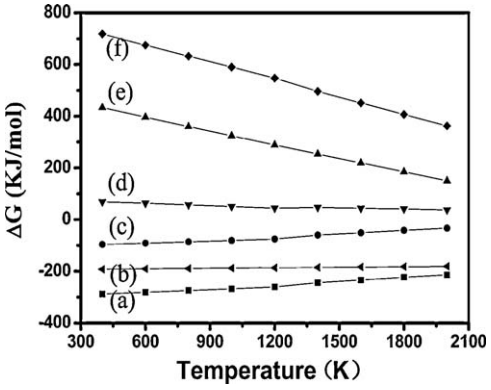

Fig. 1. The curve of relationship of Gibbs free energy and temperature. (a) $ZrO_2 + C + 2Mg = ZrC + 2MgO$; (b) $Zr + C = ZrC$; (c) $ZrO_2 + 2Mg = Zr + 2MgO$; (d) $2Mg + 3C = Mg_2C_3$; (e) $ZrO_2 + C = Zr + CO_2$; (f) $C + 2MgO = 2Mg + CO_2$.

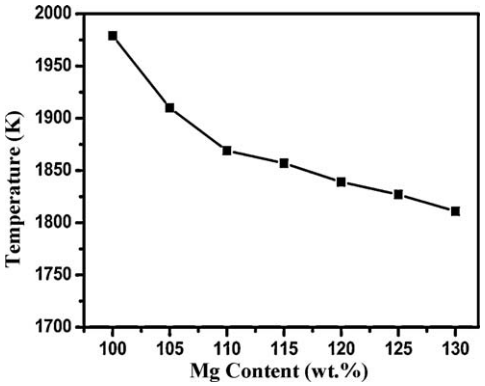

Fig. 2. Effect of Mg (154 μm) content on combustion temperature.

metallic Mg boils and partly evaporates, which leads to the loss of elemental Mg and impair the purity of final ZrC powder.

Fig. 2 shows the effect of Mg (154 μm) content on combustion temperature. The highest combustion temperature observed is 1979 K, which decreases rapidly as the amount of Mg increases, when Mg content is less than 110% (the excessive mass fraction of Mg is 10% on the basis of stoichiometric proportion, the same below). As Mg content increases further, the decrease slows down. The decrease of combustion temperature can be explained that as the increase of Mg content, the evaporation of Mg increases and absorbs more energy.

XRD pattern of samples with different Mg (154 μm) content shows presence of ZrC as a major phase together with MgO and ZrO_2 phases (Fig. 3a). The presence of ZrO_2 phase in the XRD

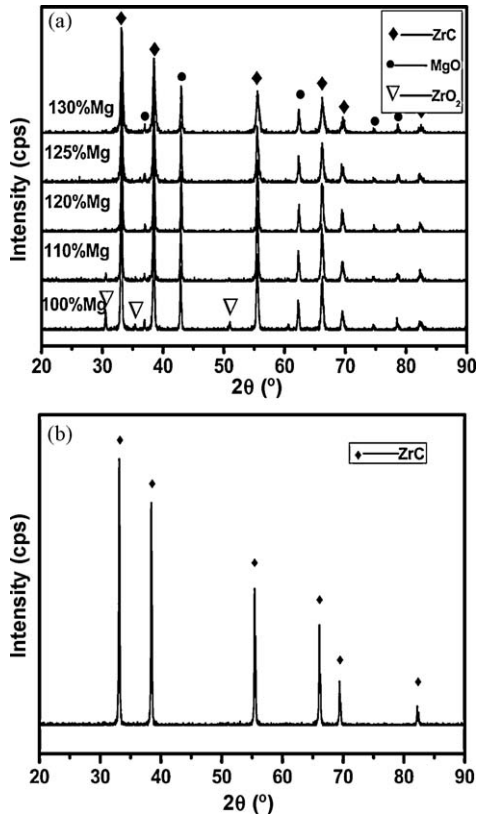

Fig. 3. XRD patterns of SHS samples (a) with different Mg (154 μm) content before acid-washing; (b) with 120% Mg content after acid-washing.

pattern of the synthesized product indicates incomplete conversion. When Mg content is 120%, the residual ZrO_2 phase disappears. After acid-washing, XRD pattern of the sample with 120% Mg shows only ZrC phase (Fig. 3b). It is concluded that complete conversion of the reactants into products is obtained in the sample with 120% Mg. Oxygen analyzer shows that the oxygen content of the product is 3.43%.

Fig. 4a is the SEM image of the sample with 120% Mg (154 μm) before acid-washing. The product is highly porous and consists of two typical morphologies: the big disc shape and fine grains. The disc shape particles are distributed on the fine grain surface and identified to be MgO particles, whereas fine grains are identified to be ZrC particles. To remove MgO, the sample is treated by acid-washing and the FESEM image is shown in Fig. 4b. It reveals that most particles show nearly spherical structure and the particles are characterized by a relatively narrow size distribution. Particle size distribution of the final powder is shown in Fig. 5 and the mean particle size is 320 nm.

The TEM images of ZrC powder show the presence of mainly spherical particles and further prove its mean particle size of about 300 nm (Fig. 6a). Fig. 6b shows that there are some defects located in the crystal lattice (noted by arrows). It is believed that concentrations of lattice defects in the products

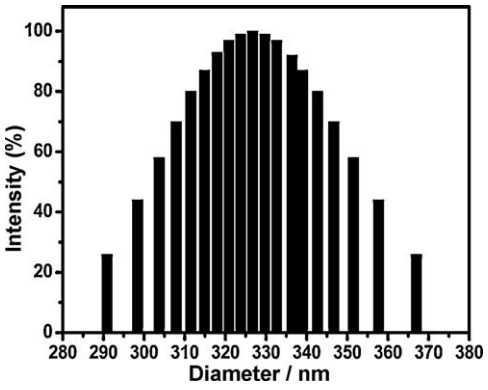

Fig. 5. Particle size distribution of the acid-washed ZrC powders obtained with 154 μm Mg particles.

can be ascribed to high exothermicity of the process and very high rates of heating and cooling of the reaction zone.

The particle size has great influences on the reaction activity of Mg particles. The finer is the Mg particles, the higher is the reaction activity, and the combustion temperature. When Mg particle is finer, the specific surface area increases, surface contact area between Mg and ZrO_2 increases and leads to more complete conversion of the reactants into products.

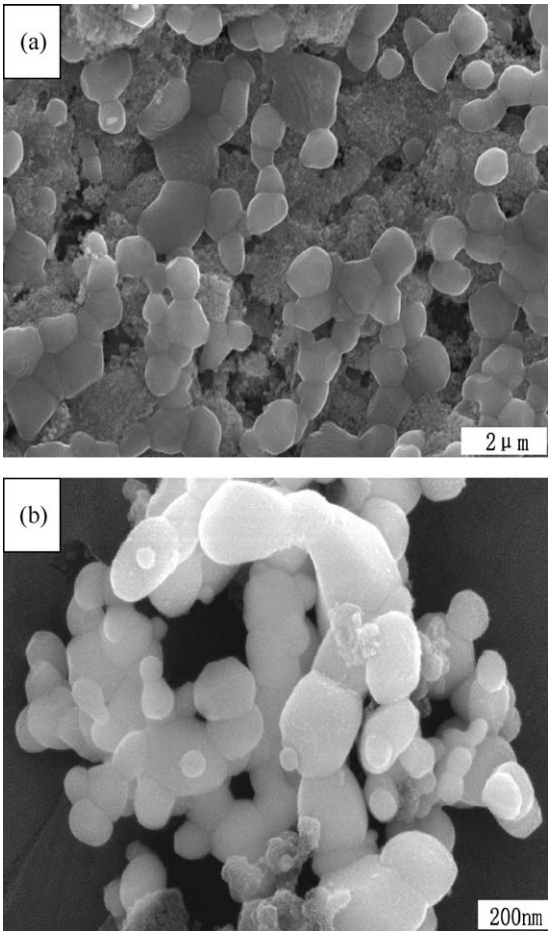

Fig. 4. Micrographs of SHS sample with 120% Mg (154 μm) (a) SEM image of sample before acid-washing; (b) FESEM image of sample after acid-washing.

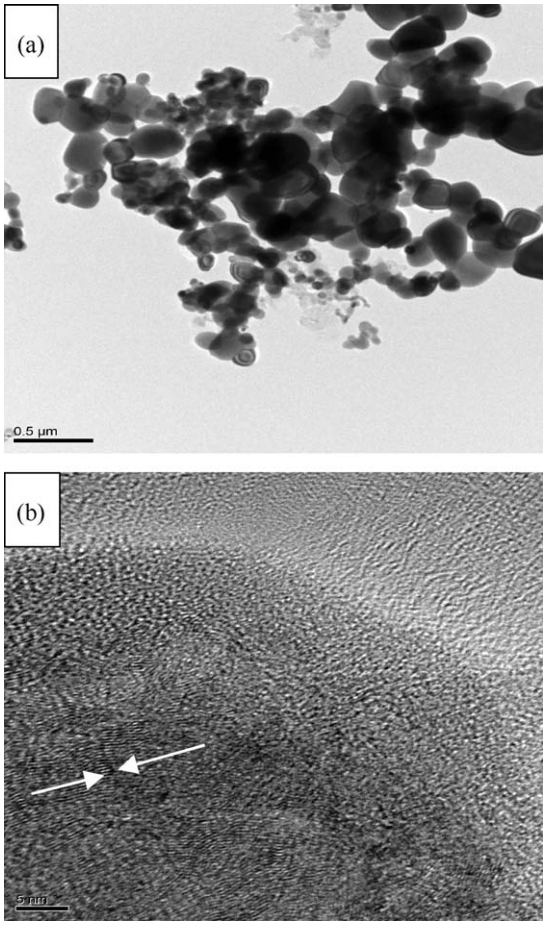

Fig. 6. TEM images of the acid-washed ZrC powder obtained with 154 μm Mg particles.

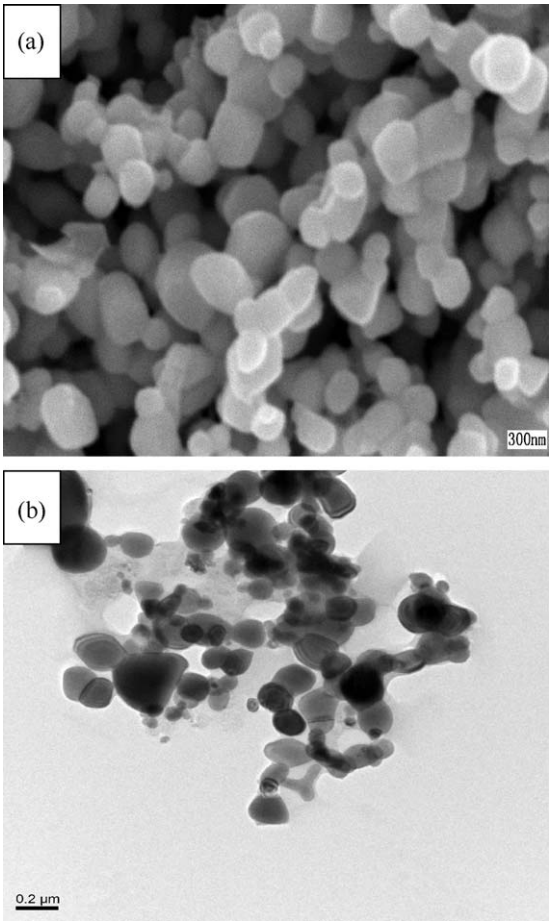

Fig. 7. SEM and TEM image of the acid-washed ZrC powders obtained with 74 μm Mg particles.

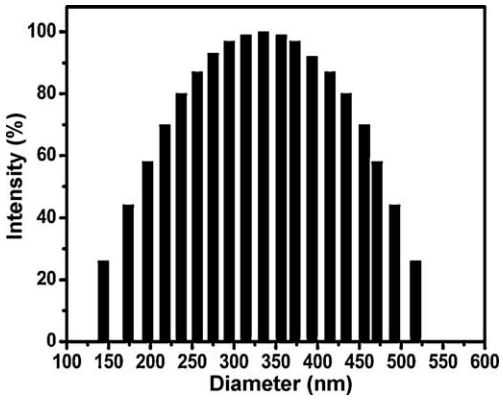

Fig. 8. Particle size distribution of the acid-washed ZrC powders obtained with 74 μm Mg particles.

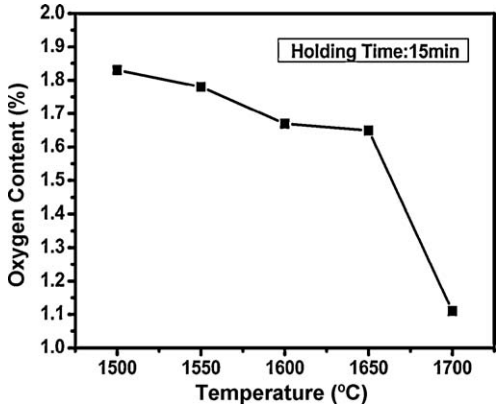

Fig. 9. Effect of the post-heat treatment temperature on oxygen content.

The results show that when the particle size of Mg is 74 μm and the content is 120%, ZrC powders has a higher purity than using 154 μm particles. Oxygen analyzer shows that the oxygen content is 3%. Fig. 7 is the SEM and TEM images of ZrC powders obtained with 74 μm Mg particles. Particle size distribution of ZrC powder is shown in Fig. 8. It is noted that the mean particle size is 335 nm, which reveals the grain size seems to be independent of the particle size of Mg due to its liquid form during combustion process.

ZrC has a NaCl structure, which is metastable, not an equilibrium structure. Both the Zr atoms and the carbon atoms are located in fcc sublattices, but the vacancies are present only in the carbon sublattice in ZrC, with a vacancy concentration ranging from a few percent to more than 50% [14]. Research shows that stoichiometric ZrC does not exist and moreover, ZrC is easier to be oxidized. It is recognized that atomic oxygen can be substituted for the carbon present in the interstitial vacancies of the ZrC lattice, forming $Zr(C_xO_y)$, and up to 60% of the interstitial position can be filled by atomic oxygen [15]. The research of Shimada and Ishii also shows that the oxygen uptake is largely used in oxidation of Zr in ZrC, not in the removal of all carbon as carbon dioxide [16]. In order to promote further reduction of $Zr(C_xO_y)$ and decrease oxygen content, post-heat treatment is applied to the product obtained by SHS process.

In the present study, samples synthesized by SHS with 120% Mg (74 μm) were heat treated by Spark Plasma Sintering (SPS) method. Before being treated, extra Mg (20% of the total amount) was added to the sample. The effect of temperature and holding time on oxygen content of the final product are shown in Figs. 9 and 10 respectively.

As the temperature increases from 1500 °C to 1700 °C, the oxygen content decreases from 1.83% to 1.11%. It may due to the reduction abilities of Mg and free carbon increase at higher temperature.

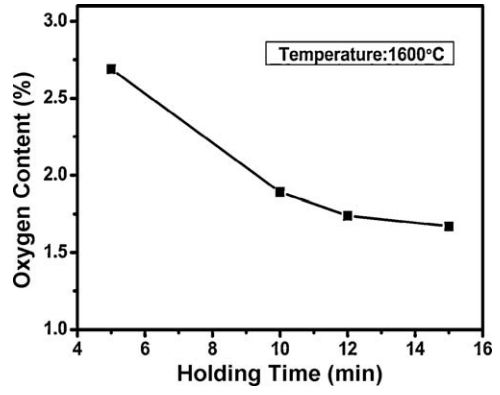

Fig. 10. Effect of the post-heat treatment holding time on oxygen content.

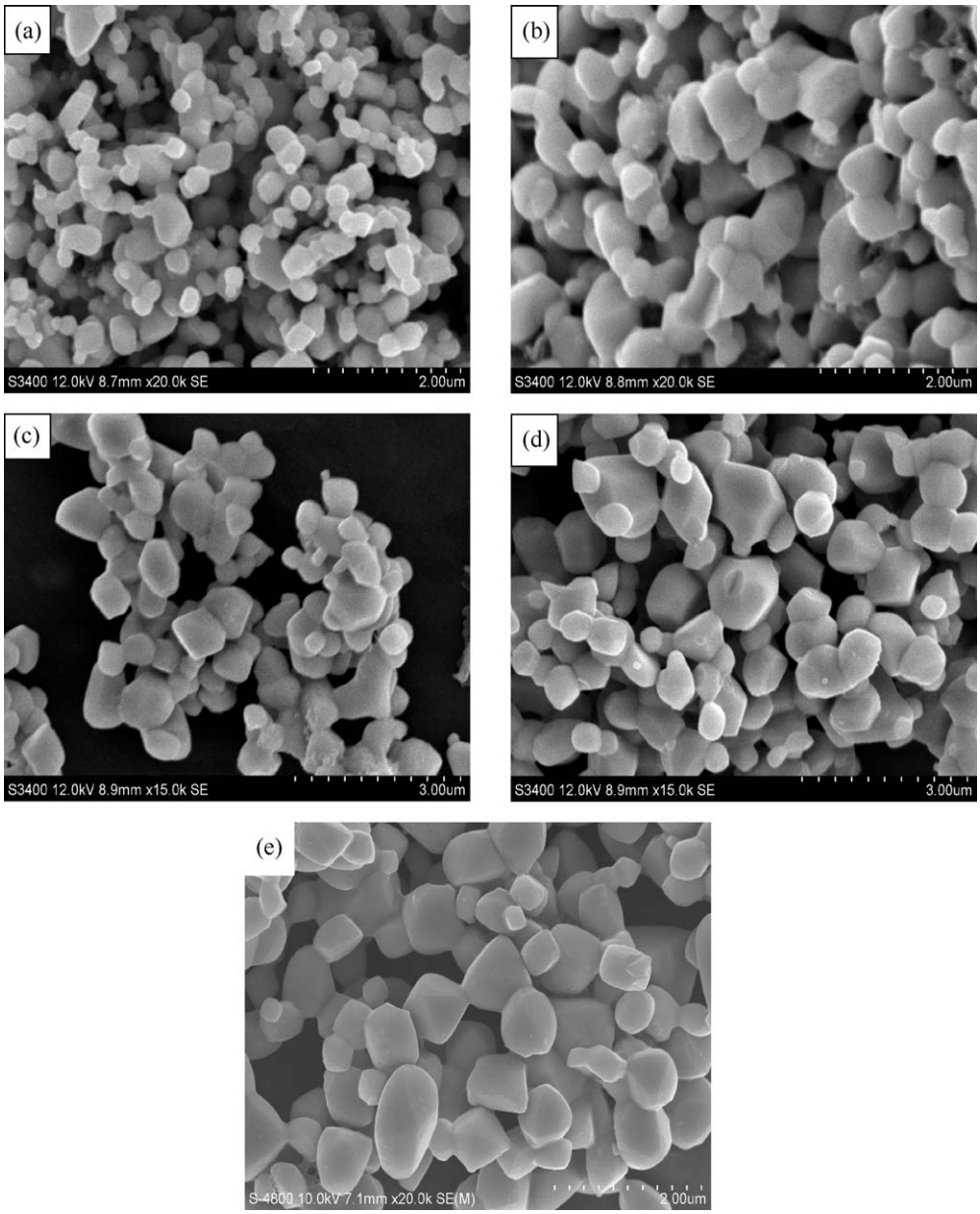

Fig. 11. SEM image of SHS sample heat treated by different temperature with holding time of 15 min (a) 1500 °C; (b) 1550 °C; (c) 1600 °C; (d) 1650 °C; (e) 1700 °C.

Fig. 10 reveals that the oxygen content decreases significantly with the increase of holding time. Fig. 11 shows the SEM image of the sample treated at different temperatures with holding time of 15 min. It is noted that the mean particle size remains at about 300 nm, when the temperature is 1500 °C. With further increase of temperature the grain grows and up to 800 nm when the temperature applied is 1700 °C.

4. Conclusion

(1) ZrC fine powder had been prepared by self-propagating high-temperature synthesis (SHS) based on exothermic reduction reaction of ZrO_2–C–Mg system.
(2) The combustion temperature decreases as the increases of Mg content. When Mg content is 100%, the highest combustion temperature observed is 1979 K. Mg content plays an important role in the synthesized products. The complete conversion of the reactants into products is obtained in samples with an excessive addition of Mg (20% excessive addition).
(3) When the particle size of Mg is 74 μm, ZrC powder has a lower oxygen content than using 154 μm Mg particles. The ZrC powder has lower oxygen content (3%) from 74 μm Mg raw powder than that (3.43%) from 154 μm Mg raw powder, while the grain size remains about 320 nm, which seems to be independent of the particle size of Mg.
(4) As the post-heat treatment temperature increases from 1500 °C to 1700 °C, the oxygen content of ZrC powder decreases from 1.83% to 1.11%, while the particle size increases from 300 nm to 800 nm.

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