Synthesis of ZrC Nanoparticles in the ZrO₂–Mg–C–Fe System Through Mechanically Activated Self-Propagating High-Temperature Synthesis

Abdollah Hajalilou · Mansor Hashim · Halimah Mohamed kamari · Kazem Javadi · Samikannu Kanagesan · Mohammad Parastegari

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Abstract ZrC nanoparticles in the matrix of Fe were produced by the mechanically activated self-propagating high-temperature method using ZrO₂/C/Mg/Fe powder mixtures. The effects of milling time, Fe content, and combustion temperature as well as the formation route for synthesizing ZrC powder particles were studied. The samples were characterized by XRD, SEM, TEM, and DTA. The XRD results revealed that, after 18 h of mechanical activation, ZrO₂/ZC/Mg/Fe reacted with the self-propagating combustion (SHS) mode at 870 °C producing the ZrC–Fe nanocomposite. It was also found that both mechanical activation and Fe content played key roles in the ZrC synthesis temperature. With a Fe content of (5–40) wt%, the SHS reaction proceeded favorably and both the ZrC formation temperature and the adiabatic temperature (T_{ad}) decreased. The MgO content was removed from the final products using a leaching test process by dissolving in hydrochloric and acetic acids.

KEY WORDS: Mechanical activation (MA); Combustion synthesis; Fe–ZrC composite; Leaching process

1 Introduction

Zirconium carbide possesses a structure similar to that of NaCl, the carbon atoms in this compound must be located

at octahedral positions and Zr atoms at FCC locations. The compound also exhibits both metal and ceramic traits due to a mixture of ionic, covalent, and metallic bondings [1, 2]. Due to its desirable physical and chemical properties such as high melting point, hardness, good corrosion properties at high temperatures, outstanding chemical stability, low work function (4.0 eV), zirconium carbide offers an excellent choice for application in high performance cutting tools and abrasives, armored vehicles, electronic systems, and as reinforced particles in composites [3–7].

Metal matrix composites with ceramic particle reinforcements like TiC and ZrC enable relatively inexpensive, wear-resistant materials to be manufactured. Fe-based metal matrix composites reinforced with TiC particles have been regarded as suitable examples in this category of materials [8]. Most researchers have produced iron-matrix composites including TiC as a reinforcement using the powder metallurgy [9], conventional melting, and casting methods [10–14]. However, these techniques have their own limitations and sometimes require a vacuum

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A. Hajalilou (✉) · M. Hashim · S. Kanagesan
Materials Synthesis and Characterization Laboratory, Institute of
Advanced Technology (ITMA), University Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia
e-mail: e.hajalilou@yahoo.com

H. M. kamari
Physics Department, University Putra Malaysia, 43400 UPM
Serdang, Selangor, Malaysia

K. Javadi
Irankhodrow Industry, Mechanical Testing Laboratory, Tehran,
Iran

M. Parastegari
Materials Synthesis and Characterization Laboratory, Isfahan
University of Technology, Isfahan, Iran

atmosphere and a high-temperature furnace. Therefore, according to our previous investigation on the production of TiC nanoparticle through the mechanical activation process [15, 16], it was found that the mechanical activation remarkably reduced the synthesis temperature. Thus, for this same purpose, a mechanically activated self-propagating high-temperature (MASHS) technique has been developed for obtaining powder nanocomposites consisting of an iron matrix and ZrC nanometer particles as the reinforcing phase. This method involves the following consecutive processes: short-time mechanical activation of the mixture of powder reagents in a high-energy planetary ball mill, self-propagating high-temperature synthesis, and additional mechanical activation of the synthesis products.

Another aspect of the study is the investigation of the effect of mechanical activation on SHS reaction based on both experimental observations and thermodynamic calculations. Finally, the effect of iron content on the synthesis temperature of ZrC in the matrix of iron has been investigated.

2 Materials and Method

Table 1 presents the characteristics of the raw materials used for the synthesis of ZrC ceramic particles and Fe–ZrC composite. The specimens were prepared with ZrO₂/Mg/C/Fe at a ratio based on that of the stoichiometric ZrC plus (0–90) wt% Fe in the ZrO₂/Mg/C/Fe powder mixtures.

A high-energy (planetary) ball mill was performed for mixing the reactant powders for various durations from 0 up to 30 h at room temperature under an argon atmosphere. A ball-to-powder weight ratio of 20:1 was selected. The mill had four vials each 45 mm in radius, with the vial and disk rotational speeds set at 600 and 400 r/min, respectively, to give a ratio of 600/400 between the two rotational speeds. For ball milling, four zirconia balls 18 mm in diameter and 3 zirconia balls 12 mm in diameter were employed. The energy of the ball mill could be elevated using a distribution of balls with diverse sizes. Ball size distribution intensifies the frequency of the ball–ball and ball–wall impacts to yield a higher ball mill energy [17].

Table 1 Properties of the raw materials used

Powder	Average particle size (μm)	Purity (wt%)	Supplier
ZrO ₂ (zirconia)	<50	99.9	Merck (P.N. 1089170100)
Mg	<46	99.9	Merck (P.N. 1087120005)
C (graphite)	<50	99.9	Merck (P.N. 1042062500)
Fe (iron)	<120	99.9	Merck (P.N. 1038151000)

Subsequently, pellet shape specimens, 24 mm in diameter and 8 mm in thickness, were fabricated in a steel-die using a load of 29.4 kN. The SHS tests were performed in a vacuum vessel full of argon. The reaction was ignited by a tungsten arc heating established under the compact.

Differential thermal analysis (DTA) (TGA/SDT A851E/LF1600/MT5/347) was used to study both the exothermic reaction behavior and to estimate ignition temperature. About 25 mg of the activated powder was held in Pt crucible and heated to 1,000 °C at a rate of 20 °C/min. Also, in a vacuum vessel filled with argon, the copper-mold-aided combustion front quenching conduct experiment was executed with 30 wt% Fe in a 60 mm × 8 mm × 2 mm compact.

X-ray diffractometry (XRD) equipped with the High Score Software in a Philips X' PERT MPD diffractometer was applied using a filtered CuK_α radiation ($\lambda = 0.15406$ nm) to evaluate the phase transformation and mean crystallite size of powder particles. Average crystallite size and internal lattice strain were computed by broadening the XRD peaks using the following Williamson–Hall Equation [18].

$$b \cos \theta = 0.9\lambda/d + 2\sqrt{\varepsilon^2} \sin \theta,$$

where d is the mean crystallite size, ε is the mean internal strain, θ is the Bragg's diffraction angle, λ is the wavelength of the radiation used, and b is the diffraction peak width at half maximum intensity.

Scanning electron microscopy (SEM) and transmitted electron microscopy (TEM) were used to study the morphology and structure of the powder particles. Finally, hydrochloric acid (HCl) and acetic acid were used as solvents for removing the unwanted compounds to achieve a pure Fe–ZrC composite.

Fig. 1 XRD patterns of ZrO₂/Mg/C/5 wt% Fe powder mixture ignited at different temperatures without mechanical activation (ZrO₂ (monoclinic) (filled square), ZrO₂ (tetragonal) (open square), MgO (filled triangle), Fe₂O₃ (filled circle))

3 Results and Discussion

3.1 Structural Evolution

The effect of mechanical activation on the synthesis temperature was investigated by performing the experiment on the samples including 5 wt% Fe under two different conditions: (1) ignition at different temperatures without mechanical activation, and (2) ignition at 870 °C after mechanical activation over different periods. Figure 1 shows the XRD patterns of the specimens ignited at 870, 1,260, and 1,360 °C without mechanical activation.

The XRD peaks of ZrO₂ (monoclinic), MgO, and Fe₂O₃ were observed after ignition at 870 °C. When the ignition temperature was raised to 1,260 °C, the Fe₂O₃ peaks disappeared and the monoclinic phase structure of ZrO₂ changed to a tetragonal one. Most notably, no zirconium carbide peaks were observed. By increasing the ignition synthesis temperature to 1,360 °C, the only noticeable change was a small reduction in the number of peaks and an increase in their intensity, which implies the increasing amounts of crystalline powders. This indicates that, despite ignition at high temperatures, the desired ZrC phase did not form in those samples that had not been mechanically activated.

Figure 2 shows the XRD patterns for powder mixtures ignited at 870 °C for 7 min with different activation times. No peaks of the ZrC phase are observed in the initial powders after 6 h of activation, suggesting that activation times higher than 6 h are needed for the synthesis of ZrC. When the process was continued up to 12 h, the width of the peak increased due to the fine crystallite size but their intensity decreased because of the increase in lattice strain. When the activation time was increased from 12 to 18 h, the ZrC peaks, although weak and not significant, appeared. In fact, it may be assumed that the combustion reaction led to the formation of ZrC due to the energy stored in the powder mixtures during 18 h of activation. The low intensity of the peaks, however, suggests an incomplete reaction. Increasing activation time from 18 to 24 h led to the formation of Fe₂Zr with more pronounced ZrC peaks. Moreover, a noticeable conversion was that of the monoclinic ZrO₂ structure to a cubic one. ZrO₂ may appear in one of three crystal structures depending on the temperature. Below 1,170 °C, it assumes a monoclinic structure; between 1,170 and 2,370 °C, it exhibits a tetragonal structure; and above 2,370 °C, it has a cubic structure [19]. Conversion of the ZrO₂ structure to the cubic form as a result of increased activation time to above 18 h indicates that the adiabatic temperature must have reached 1,800 K and above [16] such that the combustion reaction between the reactants occurred almost completely. By extending the activation time to 30 h, the ZrO₂ peaks completely vanished but a small amount of MgO phase

Fig. 2 XRD patterns taken from an initial powder mixture with 5% iron ignited at 870 °C after different mechanical activation times (ZrO₂ (monoclinic) (filled square), ZrO₂ (tetragonal) (open square), ZrO₂ (cubic) (open circle), MgO (filled triangle), Fe₂Zr (filled club), Fe (filled diamond), ZrC (filled inverted triangle))

could still be observed in the final products. The ZrC crystallite size was found to be about 38 nm.

3.2 DTA Analysis

Thermal behavior of 24 h-activated powder was examined by simultaneous thermal analysing (STA) technique. Figure 3 shows the DTA and DSC curves of the sample with 5 wt% Fe activated for 24 h. According to this figure, it seems that the combustion reaction started to ignite at around 592 °C. Further increase in temperature during heating in the calorimeter caused the occurrence of an exothermic peak at around 638 °C. This may be attributed to the reduction of ZrO₂ by Mg. A mountain-like endothermic peak was observed at around 790 °C in the DTA curve. This indicates a reduced reaction rate as a result of the primary reaction products (MgO and Zr) on the surface of the reactants. This may also be related to the allotropic change of Fe (α) to Fe (γ). Eventually, the heat released from the formation of such intermetallic phases as Fe₂Zr led to an increased temperature of the system. This, in turn, increased the rate of diffusion of the reactants in each other and, as a result, led to the main exothermic peak at 844 °C in the DSC curve. Based on these results, the temperature was set to 870 °C in order to ensure that the onset of the reaction.

3.3 Thermodynamic Considerations and the Effect of Iron Content on T_{ad}

One of the most significant thermodynamic factors is the adiabatic temperature of the reaction (T_{ad}) which is defined as the maximum temperature obtained under adiabatic conditions as a

Fig. 3 DTA and DSC curves for 24 h-activated powder

result of the heat released from the reaction. According to Merzan of [20], T_{ad} should be higher than 1,800 K for the reaction to be completed based on the SHS type. The adiabatic temperature (T_{ad}) and the practical combustion temperature (T_c) of the SHS reaction can be computed by applying the thermodynamic data [21] and using the equation below.

$$-\Delta H_{298}^0 = \left[\int_{T_i}^{T_m} (C_p) dT \right] + \Delta H_m + \left[\int_{T_m}^{T_{ad}} (C_p) dt \right]$$

$$-\Delta H_{298}^0 = \left[\int_{T_i}^{T_{mp \text{ of Fe}}} (XC_p \text{ Fe(s)} + 2C_p \text{ MgO} + C_p \text{ ZrC}) dT \right] + X\Delta H_{mp \text{ of Fe}} + \left[\int_{T_{mp \text{ of Fe}}}^{T_{ad}} (C_p \text{ Fe(l)} + 2C_p \text{ MgO} + C_p \text{ ZrC}) dt \right]$$

$$\Delta H_{298}^0 (\text{ZrO}_2) = -1,100.8 \text{ kJ/mol}$$

$$\Delta H_{298}^0 (\text{ZrC}) = -207.1 \text{ kJ/mol}$$

$$\Delta H_{298}^0 (\text{MgO}) = -601.6 \text{ kJ/mol}$$

$$\Delta H_{298}^0 = -309.500 \text{ kJ/mol}$$

$$-\Delta H_{298}^0 = \left[\int_{1023}^{1809} (149.11 + 28.18X) + (10.25 - 7.32X) \times 10^{-3}T - (35.65 + 2.9X) \times 10^5 T^{-2} + 25.04X \times 10^{-6} T^2 \right] + 13,800X + \left[\int_{1809}^{T_{ad}} (149.11 + 46.02X) + 10.25 \times 10^{-3}T - 35.65 \times 10^5 T^{-2} \right]$$

Figure 4 shows the calculation results for the adiabatic temperature (T_{ad}) and combustion temperature (T_c) as a

Fig. 4 Adiabatic temperature (T_{ad}) and combustion temperature (T_c) as a function of Fe content

function of iron content. As implied, T_{ad} and T_c decrease with increasing iron content. When iron addition is under 40 wt%, the T_{ad} of the Fe–ZrO₂–C–Mg system is above 1,800 K, which follows the empirical criterion suggested by Merzhanov [20], and the combustion wave will self-sustainingly promote through the whole compact once ignited by the external heat supply. As a dilution, enhanced iron content would decline the combustion temperature. When iron content rises to about 40 wt%, combustion temperature decreases to 1,755 K, thus leading to the failure of the SHS reaction in the Fe–ZrO₂–Mg–C reactant powders. Generally speaking, due to the unavoidable heat loss during SHS processing, the practical combustion temperature is usually lower than its corresponding theoretical adiabatic temperature.

The calculated adiabatic temperature of a reaction among Mg, C, and ZrO₂ is about 3,219 K. Therefore, it is expected that, in the absence of any Fe content, the SHS reaction must occur and ZrC be synthesized. Hence, the samples with different Fe contents ((0–60) wt%) were activated for 24 h and ignited at 870 °C; the corresponding XRD patterns are shown in Fig. 5. As can be seen, the only distinguishable phases in the iron-free sample are those of the initial powder mixture. Moreover, the existence of MgO showed that only the reduction stage occurred and that the SHS reaction was not completed. This suggests that a small amount of iron is not only necessary for ignition but it also plays a fundamental role in the ZrC synthesis temperature. It was predicted that T_{ad} would reduce to <1,800 K with increasing amounts of iron since the heat released from the reaction would be spent on the heating of iron. The calculation of T_{ad} for different amounts of iron showed that its value would be <1,800 K for the samples containing more than 60% Fe. Figure 5c clearly shows that the absence of ZrC peaks and that the only visible phase

Fig. 5 XRD patterns taken from the initial powder mixture with 0% **a**, 20% **b**, and 60% **c** iron activated for 24 h and ignited at 870 °C (ZrO₂ (monoclinic) (filled square), ZrO₂ (cubic) (open circle), MgO (filled triangle), Fe (filled diamond), ZrC (filled inverted triangle))

Fig. 6 The equilibrium phase diagram of Fe–Zr

was iron at Bragg diffraction angles (2θ) of 44° and 62° while the rest of the peaks disappeared.

3.4 Mechanism of Synthesis

Based on the physical state of the reactants at the adiabatic temperature, the SHS reactions may be classified in the following categories: (1) solid–solid reactions ($A(s) + B(s) = AB(s)$); (2) solid–liquid ($A(s) + B(l) = AB(s)$); (3) liquid–liquid ($A(l) + B(l) = AB(s, l)$); and (4) solid–gas (including liquid + gas) ($A(s, l) + B(g) = AB(s)$).

The molar volume change from the reactants to the products has a fundamental role. Solid–solid reactions are essentially controlled by diffusion. Wagner [22] suggested a parabolic rate function for such kinetics.

$$d\eta/dt = k/\eta,$$

Fig. 7 The equilibrium phase diagram of Zr–C

Fig. 8 XRD patterns of the 30 h-activated sample ignited at 870 °C (including 5% iron): **a** before dissolution in HCl, **b** after dissolution in HCl at a temperature of about 60 °C for 90 min (MgO (filled triangle), ZrC (filled inverted triangle))

where k is the reaction rate constant which depends on the diffusivities.

It may be concluded from the XRD analyses and the theoretical thermodynamic calculations that the process of SHS reaction between ZrO₂/Mg/C reactants includes the following stages. In the first stage of ignition, the Mg powder capillary particles melted. In the second stage, the molten Mg penetrated into the ZrO₂ pores, resulting in a reduction by Mg. The heat released from this reaction is about 122 kJ/mol since it was able to increase the system temperature to 1,426 °C. Under these circumstances, the produced zirconium (below its melting point = 1,866 °C) can only react with carbon via a diffusion mechanism to form zirconium carbide. Once the product layer forms among the reactants, further reaction proceeds by diffusion at carbon atoms across the Zr layer leading to slow reaction kinetics. The reaction mechanism of ZrC synthesis in the Mg–C–ZrO₂ system (in the absence of Fe) is similar to that of TiC in the TiO₂–Al–C system previously reported in

Fig. 9 SEM **a** and TEM **b** images of ZrC after dissolution in HCl

Fig. 10 XRD patterns of the sample with 20% iron (activation time of 24 h, ignition temperature of 870 °C): **a** before dissolution in acetic acid, **b** after dissolution in acetic acid for 90 min at room temperature (ZrO₂ (cubic) (open circle), MgO (filled triangle), Fe (filled diamond), ZrC (filled inverted triangle))

Hajalilou et al. [14]. Based on the different views reported in Ref. [23], the combustion reaction may take place once the heat released from the reaction is high enough not only to raise the system temperature to the melting point of zirconium (1,855 °C) but also to lead to the dissolution of carbon in zirconium and the precipitation of ZrC.

In the presence of Fe, the reaction mechanism would change due to the formation of Fe₂Zr in the of ZrO₂–Mg–C–Fe system. The negative enthalpy of Fe₂Zr (about –84 kJ/mol) suggests the feasibility of its thermodynamic formation at ambient temperature. According to the Fe–Zr binary diagram (Fig. 6), this phase is a relatively stable phase compared to other intermetallic compounds. ZrO₂ is prone to settling down on the surface of Fe₂Zr, which will be deleterious for wetting and interdiffusion thereby preventing the Fe₂Zr-producing reaction and reducing the associated heat liberation. Hence, the heat released from the formation of this compound can increase the system temperature. Thus, considering the Fe–ZrO₂–C–Mg

system, one would anticipate the formation of a molten eutectic iron–carbon around 1,150 °C because of the spatial adjacency of iron and carbon particles and the relatively high diffusivity of carbon atoms. This endothermic reaction is likely to be superseded by the reaction of the previously produced carbon-rich iron-liquid with the zirconium particles to produce zirconium carbide particles, which would be highly exothermic. Regarding Fig. 7, carbon could be dissolved in the molten eutectic mixture to result in the precipitation of zirconium carbide particles below 860 °C. It may be concluded from these observations that adding 5 wt% iron to ZrO₂–C–Mg reactants could encourage the reaction incidence by prior formation of an iron–carbon liquid. In this mechanism, the ratio of atomic radii, R_x/R_m , (where R_x is the radius of the small nano-metallic atom and R_y is the atomic radius of the transition metal) can directly affect not only T_{ad} but also the structure of the product and the kinetics of the reaction [24].

3.5 Leaching Process to Produce ZrC

For eliminating magnesium oxide from the sample with 5% iron activated for 30 h and ignited at 870 °C, leaching experiments were performed using a 2 mol/L HCl solution at a temperature of about 60 °C for 90 min to observe the complete omission of MgO. The XRD pattern of this sample is shown in Fig. 8. The solution reaction of the MgO in HCl acid can be expressed as follows:

To remove the extra amounts of HCl (until pH reached around 7), a filtering process was used and the purified products were washed several times before being dried in the oven at 300 K for 90 min.

The SEM and TEM images of the sample etched with HCl are presented in Fig. 9. Clearly, the ZrC particles are

Fig. 11 SEM **a** and TEM **b** micrographs of ZrC–Fe composite after dissolution in acetic acid

round in shape with a homogeneous distribution of powder particles. TEM image confirmed the nanoscale size crystalline of ZrC.

3.6 The Leaching Process to Produce Fe–ZrC Composite

To produce the Fe–ZrC composite through the elimination of MgO from the final products, a suitable solvent with no influence on Fe and ZrC must be used. For this purpose, acetic acid was chosen and the dissolution process was carried out for 90 min at room temperature. Figure 10 shows the XRD patterns for the sample with 20 wt% Fe, 24 h activation, and ignition at 870 °C before and after dissolution. As can be seen, magnesium oxide peaks completely disappeared after the dissolution process. However, the decreasing intensity of iron peaks suggested that a small amount of iron was dissolved in acetic acid. Controlled temperature and time make it possible to decrease the iron content to its minimum and to eliminate ZrO₂ as well. The SEM and TEM images for this sample are shown in Fig. 11.

4 Conclusions

Mechanically activated self-propagating high temperature synthesis method was used to fabricate zirconium carbide and its composite with Fe in the presence of Mg and ZrO₂. XRD results showed that ignition temperatures of up to 1,360 °C were not sufficient for starting the combustion reaction among the reactants. Thus, activation energy was needed to provide either thermally (using an ignition agent like Fe) or mechanically (by collision of the powders to cause reaction between them). Additionally, the results suggested that the effect of iron (5%) was more effective than 18 h of mechanical activation in decreasing ignition

temperature. Moreover, the ZrC formation mechanism was changed by introducing about 5% iron. The addition of iron resulted in enhanced reaction kinetics by forming a molten eutectic (Fe–Zr). However, iron (Fe) contents above 40% could not be used in the SHS mode. Finally, the MgO and ZrO₂ were eliminated by dissolving in HCl and in acetic acid as well as by process control.

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