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RESEARCH

Thermodynamic study of zirconium carbide synthesis via a low-temperature pyrovacuum method

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Abstract

In this research, the thermodynamic aspect of the nano-sized zirconium carbide production is investigated via a facile, low-temperature and cost-effective carbothermal method under vacuum and argon atmospheres. The starting materials were zirconium acetate and sucrose as zirconium and carbon precursors, respectively. The gels were prepared based on 3, 4, 5, and 7 molar ratios of carbon to zirconium and heated at 1200 and 1400 °C under vacuum and argon atmospheres. The formation of zirconium carbides under different atmospheres were studied via thermogravimetric analysis and the results were compared. The phase composition and microstructural features were investigated using X-ray diffraction and scanning electron microscopy, respectively. According to the thermogravimetric results and performed thermodynamic calculations, it was revealed that the ZrC formation starts at 1200 °C under vacuum. It is also demonstrated that the formation of nano ZrC powder with crystallite sizes smaller than 30 nm, completely occurs after processing at 1400 °C in vacuum. The measured lattice parameter value of the optimized sample was equal to 4.7003 Å.

Keywords Zirconium carbide · Carbothermal reduction · Pyrovacuum · Thermo-gravimetry · X-ray diffraction

Introduction

Zirconium carbide (ZrC) is an ultra-high temperature ceramic material with superior hardness, refractoriness, electrical, and thermal properties [1]. Such as most of the refractory transition metal carbides (TaC, TiC, and HfC), ZrC is also a good candidate for high-temperature applications because of its extreme melting point (over 3000 °C), solid phase stability, and notable high-temperature thermochemical and thermomechanical behaviors [2, 3]. The carbothermal reduction of zirconia and formation of ZrC generally happen in 3 steps: (1) a solid state reaction between ZrO_2 and carbon and the formation of $CO_{(g)}$; (2) the formation of an oxy-carbide phase (ZrC_xO_y); and (3) the oxygen substitution by carbon in the ZrC_xO_y structure [4, 5]. Several carbothermal reactions have been studied to produce ZrC using various raw materials and precursors. In some cases, the addition of Na, Mg, and Al was investigated as a reducing agent in the production of ZrC from ZrO_2 or $ZrCl_4$ by combustion synthesis [6–10]. ZrC is conventionally produced via the carbothermal reduction of ZrO_2 at high temperatures (> 1600 °C). It is known that prior to carbothermal reduction, starting materials are oxidized to form monoclinic or tetragonal ZrO_2 phases [11–13]. It is assumed that the carbothermal production of carbides under vacuum (also called as pyrovacuum method) would decrease the formation temperature and oxygen content of the final products due to the reduction of oxygen partial pressure. The pyrovacuum synthesis of some common refractory carbides, such as SiC [14] and TiC [15, 16] were previously investigated. However, there are few studies on the carbothermal reduction of ZrC via pyrovacuum method [17, 18]. Sevastyanov et al. [18] investigated the effect of vacuum on the carbothermal reduction of Ti, Zr, and Hf in order to prepare nano-crystalline transition metal carbide powders.

In the present research, zirconium acetate is used as a metal precursor to produce nano ZrC using carbothermal reduction under argon and vacuum atmospheres. The main goal of this work is to study the thermodynamic aspect of carbothermal

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reduction of zirconia under pyrovacuum condition. In addition, the formation of carbide phase is investigated at different temperatures and atmospheric conditions via thermogravimetric, X-ray diffraction, and microstructural characterizations. The thermodynamic data of the pyrovacuum process was also calculated and compared with the experimental results of thermogravimetric analyses.

Materials and methods

All chemicals were purchased as analytical grades and used without further purification. Zirconium acetate (22 wt.% aq. solution) was used as metal alkoxide (Astron, Australia). Sucrose ($C_{12}H_{22}O_{11}$), polyvinyl alcohol (PVA, 160,000) and nitric acid (65 wt.%) were obtained from Merck, Germany. By considering the reactions of carbon and zirconium and the decomposition of sugar, the samples were designed in a way to produce 3, 4, 5, and 7 molar ratios of carbon to zirconium (C/Zr) and labeled as CZr3 (stoichiometry), CZr4, CZr5, and CZr7, respectively. Sucrose and PVA were dissolved in distilled water, and then zirconium acetate was added to the solution. After 15 min of stirring, the pH was adjusted to 1 by drop-wised addition of nitric acid. The solutions were heated and mixed to form viscous brownish gels. After drying in an oven at 200 °C for 4 h, the dried gels were ground using an agate mortar and passed through a 200 mesh sieve to obtain homogenous powders. Samples were then heated separately in argon (20 ml min^{-1} flow rate) and vacuum (10^{-6} mbar) at 1200 °C and 1400 °C for 3 h with the heating rate of 10 °C min^{-1} in a tube furnace using alumina crucibles. After firing, the products were fine-milled using an agate mortar to break up the large agglomerates and to obtain homogenous powdered samples. The ZrC formation mechanism was studied via thermogravimetric analysis of the CZr4 dried gel under vacuum and argon atmospheres. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained using a STA 503 thermal analyzer (BAHR, Germany), under argon (flow rate of 10 ml min^{-1}) and vacuum (10^{-6} mbar) atmospheres up to 1450 °C with a heating rate of 10 °C min^{-1} and using alumina crucibles. The phase compositions were characterized using X-ray diffraction (XRD, Cu Kα, 40 mA, 40 kV, PW1800 Philips, The Netherlands). The microstructure and morphology of the gold-coated samples were investigated using scanning electron microscopy (SEM, VEGAII XMU 2004, TESCAN, Czech Rep.). The apparent crystallite sizes were measured from the Scherrer formula according to Eq. (1) [19]. In this equation, λ is the X-ray wavelength (0.15406 nm), k is a constant (0.9), θ_o is the Bragg angle, L is the crystallite size (in nm), and β is the peak full-width at half-maximum intensity (FWHM).

$$\beta(2\theta) = \frac{k\,\lambda}{L\,\mathrm{Cos}\theta_0} \quad (1)$$

Results and discussion

Zirconium carbide formation in argon

Figure 1 demonstrates the thermogravimetric curves of CZr4 sample (stoichiometry one) which was heated in argon up to 1450 °C. As the TG curve shows, there is a major mass loss at around 300 °C which could be attributed to the decomposition of sucrose [20].

The sample's mass loss at the initial pyrolysis step (< 400 °C) is equal to 37 wt.%. The carbothermal reduction of oxides generally starts at around 800 °C in argon and a similar occurrence was reported for ZrO_2 [21]. In their research, the mass loss at 790 °C was attributed to the initial step of the carbothermal reduction [21]. For this step, Berger et al. [22] presented a mechanism in which $CO_{(g)}$ is generated after the

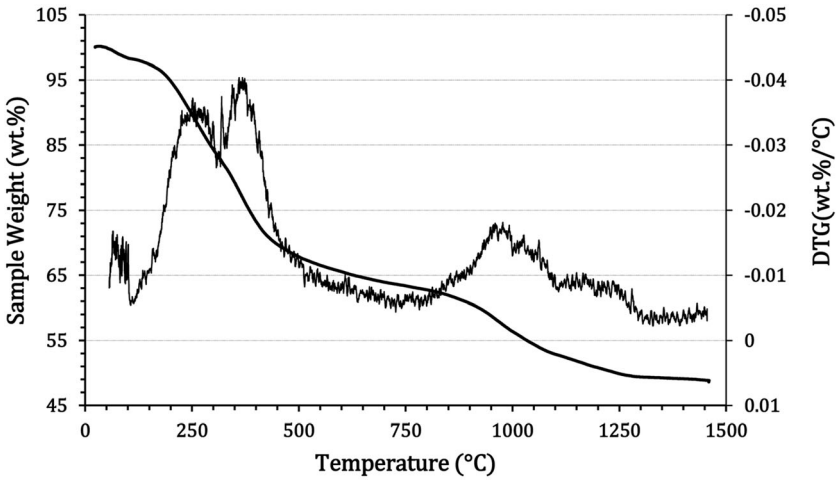

Fig. 1 Thermogravimetric curves of CZr4 sample heated in argon

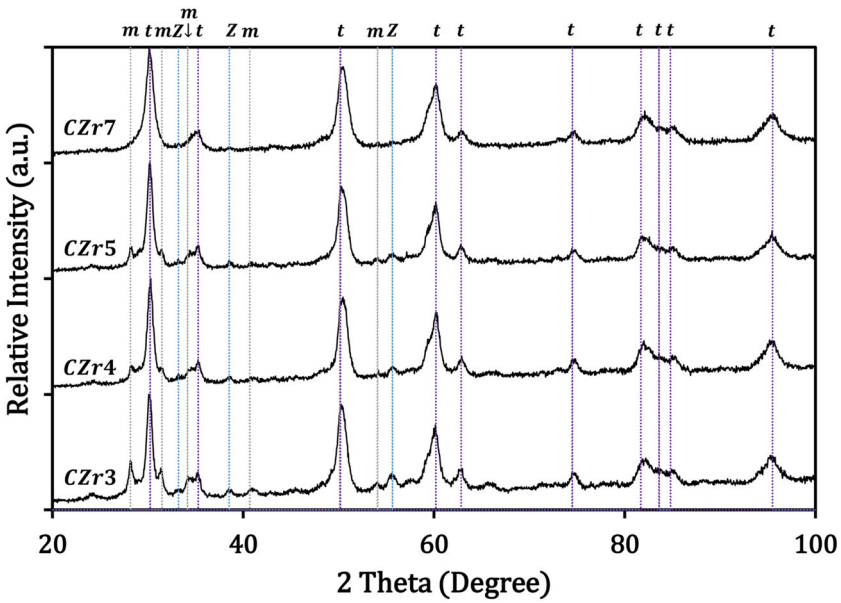

Fig. 2 XRD patterns of samples heated in argon at 1200 °C (m: m-ZrO_2, t: t-ZrO_2, z: ZrC)

reaction of carbon and oxygen on the surface of ZrO_2 particles (reaction Eq. (2)). By releasing $CO_{(g)}$, due to the significant activity of the zirconia phase, the reduction process can occur at temperatures lower than 800 °C (reaction Eq. (3)). In these equations, K refers to the equilibrium constant of the reaction at the specific temperatures.

$$ZrO_2 + C \rightarrow ZrO_{(g)} + CO_{(g)} \qquad T = 800°C,\ \log(K) = -31.925 \tag{2}$$

$$ZrO_2 + 4CO_{(g)} \rightarrow ZrC + 3CO_{2(g)} \qquad T = 800°C,\ \log(K) = -16.985 \tag{3}$$

David et al. [23] explain another mechanism for the carbothermal reduction of zirconia. They declared that, ZrO_2 decomposes to $ZrO_{(g)}$ and O_2 (reaction Eq. (4)), where O_2 would react with the existing carbon source in the matrix (reaction Eq. (5)). Then the $ZrO_{(g)}$ reacts with $CO_{(g)}$ and, finally, the solid phase of ZrO_xC_y would be precipitated (reaction Eq. (6)). However, in the second step (reaction Eq. (7)), the formed oxy-carbide phase loses parts of its oxygen content due to the reduction of $CO_{(g)}$ which is finally resulted in the formation of ZrC phase above 1100 °C. This could be seen according to the existing peak at this temperature in the DTG curve of Fig. 1.

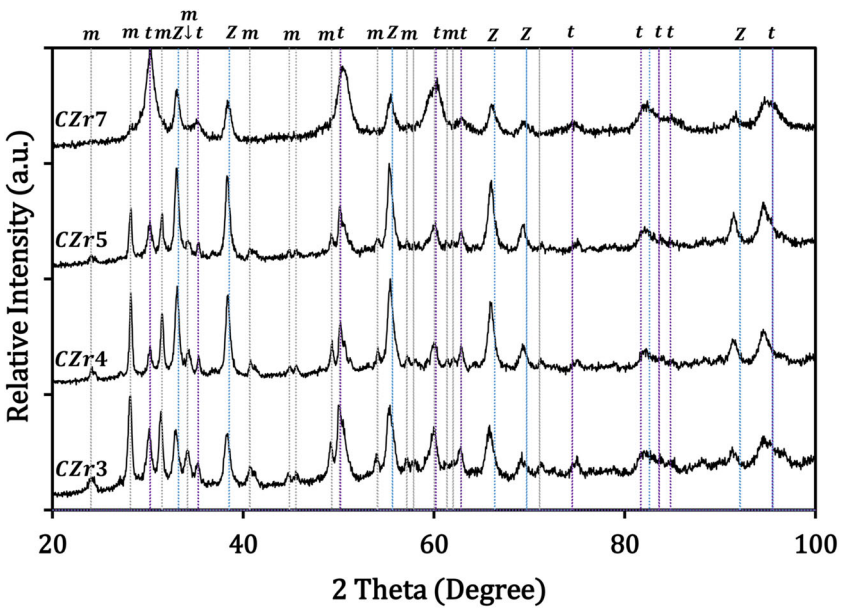

Fig. 3 XRD patterns of samples heated in argon at 1400 °°C (m: m-ZrO_2, t: t-ZrO_2, z: ZrC)

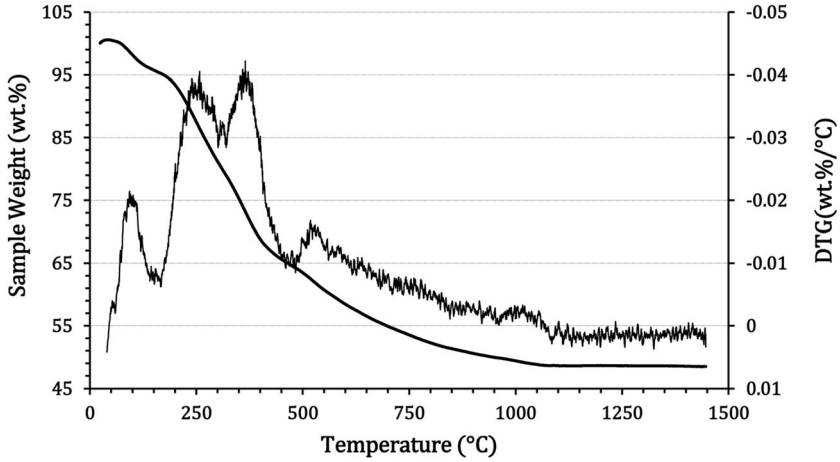

Fig. 4 Thermogravimetric curves of CZr4 sample heated under vacuum

$$ZrO_2 \rightarrow ZrO_{(g)} + \frac{1}{2}O_{2(g)} \quad T = 800°C, \ \log(K) = -83.976 \quad (4)$$

$$\frac{1}{2}O_{2(g)} + C \rightarrow CO_{(g)} \quad T = 800°C, \ \log(K) = 20.12 \quad (5)$$

$$ZrO_{(g)} + (3-3x)\,CO_{(g)} \rightarrow ZrO_xC_{(1-x)_{(s)}} + (2-2x)\,CO_{2(g)} \quad (6)$$

$$ZrO_xC_{(1-x)(s)} + 3x\,CO_{(g)} \rightarrow ZrC_{(s)} + 2x\,CO_{2(g)} \quad (7)$$

As this figure shows, according to the TG and DTG curves, the first step of the carbothermal reaction started at around 750 °C and accelerated at 1000 °C, which seems to follow the same mechanism. It also shows that the mass loss continues up to 1450 °C, which means that the carbothermal reaction has not been completed in argon atmosphere below this temperature.

Figure 2 shows the X-ray diffraction patterns of CZr3, CZr4, CZr5, and CZr7 samples which were heated at 1200 °C for 3 h in argon atmosphere. As this figure shows, by increasing the C/Zr ratio, the amount of the monoclinic zirconia phase (00-037-1484) decreases and the tetragonal phase (01-079-1767) increases. In addition, there is no peak of the monoclinic phase in the XRD pattern of CZr7 sample. A slight amount of zirconium carbide phase (00-035-0784) is obvious in the XRD patterns of CZr3, CZr4, and CZr5 samples.

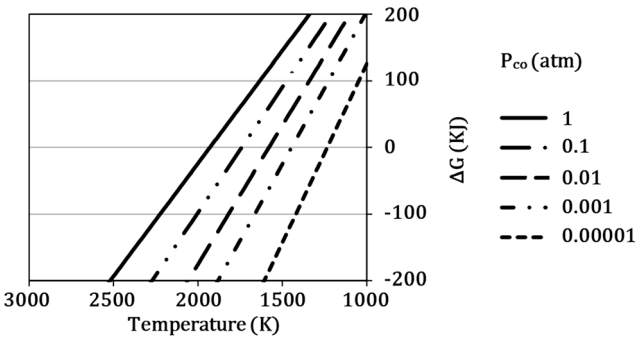

Fig. 5 Calculated ΔG values of zirconia carbothermal reduction

Figure 3 shows the X-ray diffraction patterns of CZr3, CZr4, CZr5, and CZr7 samples heated at 1400 °C for 3 h in argon atmosphere. As this figure shows, by increasing the carbon to zirconium molar ratio, the amount of the zirconium carbide phase is reduced. Since the carbon contents of CZr5 and CZr7 samples increases, the amount of the tetragonal phase increases due to a decrease in zirconia particle size after separation of zirconium ions from carbon matrix [22]. It seems that the argon atmosphere is not suitable for the complete formation of zirconium carbide at the low synthesis temperatures of 1200 and 1400 °C. As it will be discussed later, the thermodynamic condition and higher oxygen pressure may act against the full reduction of zirconia at these temperatures under argon atmosphere.

Zirconium carbide formation under pyrovacuum

Figure 4 shows the thermogravimetric curves of the CZr4 sample which was heated up to 1450 °C under vacuum. From 110 to 500 °C, the TG and DTG curves of this sample are approximately similar to those of CZr4 heated in argon. However, the first step of the carbothermal reduction started at around 550 °C under vacuum. It can be seen that the mass loss of this sample is higher than the one heated in argon, which proves that the carbothermal reaction was more progressive under vacuum condition. As this figure shows, over 1100 °C, the TG curve is almost horizontal and the DTG curve has zero value, which means that the reaction is completed. However, for the sample heated argon (Fig. 1) over 1400 °C, the DTG curve has negative values, which means that the carbothermal reduction still continues.

Figure 5 demonstrates the calculated ΔG values of the ZrO_2 carbothermal reaction at different temperatures and P_{CO} pressures. The thermodynamic data of Eqs. (8–10) are shown in Table 1 [24–27]. According to the Eq. (10), by decreasing the $CO_{(g)}$ partial pressure (P_{CO}), the ΔG values of the carbothermal reaction decrease and, hence, the reaction would

Table 1 Thermodynamic data of reactions

Phase	C_p			ΔH_f^0 (kJ mol^{-1})	ΔS_f^0 (J K^{-1} mol^{-1})	ΔG_f^0 (kJ mol^{-1})	Ref.
	a	b	c				
ZrC	36.06	0.0108	-17.95×10^5	− 207.0	33.3	− 203.5	24
ZrO_2	69.622	7.531	-1.406×10^6	− 1100	− 194.05	− 1042.7	25
C	24.43	440	-3.163×10^{-4}	---	5.73	0	26
CO	28.41	4.10	− 0.46	− 110.5	198	− 137	27

continue at lower temperatures. In this calculations, the solid phases (carbon, zirconia, and ZrC) are assumed as pure phases and their activity values were considered equal to 1 [28]. This phenomenon, i.e., decrease in carbothermal reduction temperature, was also observed in the thermogravimetric results (Fig. 4) and confirms the formation of ZrC at lower temperatures under vacuum.

Wu et al. [15] conducted a research on the carbothermal synthesis of TiC under vacuum and calculated the Gibbs free energy of TiC formation as a function of P_{CO} and temperature. The calculated values of the current research (Fig. 5), also confirm the significant effect of the applied vacuum on the carbothermal reduction of ZrO_2.

$$\Delta G_f^0 = \left[\Delta H_f^0(298) + \int_{298}^{T} \Delta C_p dT\right] - T\left[\Delta S_f^0(298) + \int_{298}^{T} \frac{\Delta C_p}{T} dT\right] \quad (8)$$

$$C_p = a + bT + cT^{-2} \quad (9)$$

$$ZrO_2 + 3C \rightarrow ZrC + 2CO_{(g)} \qquad \Delta G = \Delta G_0 + RT\ln\left(\frac{P_{CO}^2 . a_{ZrC}}{a_{ZrO_2} . a_C^3}\right) \quad (10)$$

Figure 6 illustrates the X-ray diffraction patterns of the CZr3, CZr4, CZr5, and CZr7 samples heated at 1200 °C for 3 h in vacuum. In comparison with the XRD patterns of those heated in argon at different temperatures (Figs. 2 and 3), it is obvious that the contents of zirconium carbide in the CZr4 and CZr5 samples (Fig. 6) is significant. Unlike those heated in argon, by increasing the carbon amount up to CZr6, the carbide phase increased after heating in vacuum. Figure 7 demonstrates the X-ray diffraction patterns of the CZr3, CZr4, CZr5, and CZr7 samples heated at 1400 °C for 3 h under vacuum. The amounts of the carbide phase in these samples are significantly higher than those heated in argon at the same temperature (1400 °C). It is also noticeable that the presence of zirconia phases including monoclinic, tetragonal, and cubic (00-049-1642) in the vacuum-heated samples is negligible. Cubic zirconia could be stabilized due to some oxygen vacancies [29] which is observed in samples prepared under vacuum condition at 1400 °C.

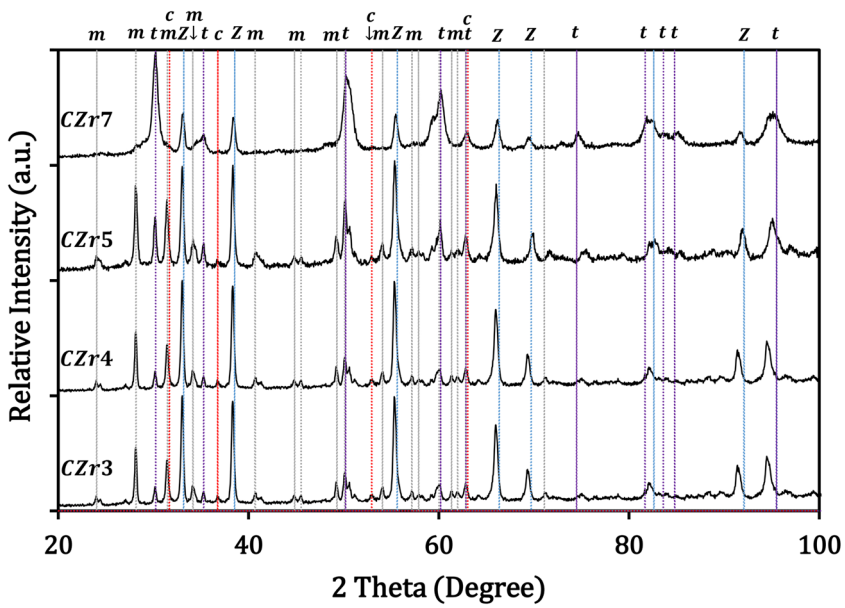

Fig. 6 XRD patterns of samples heated in vacuum at 1200 °C (c: c-ZrO_2, m: m-ZrO_2, t: t-ZrO_2, z: ZrC)

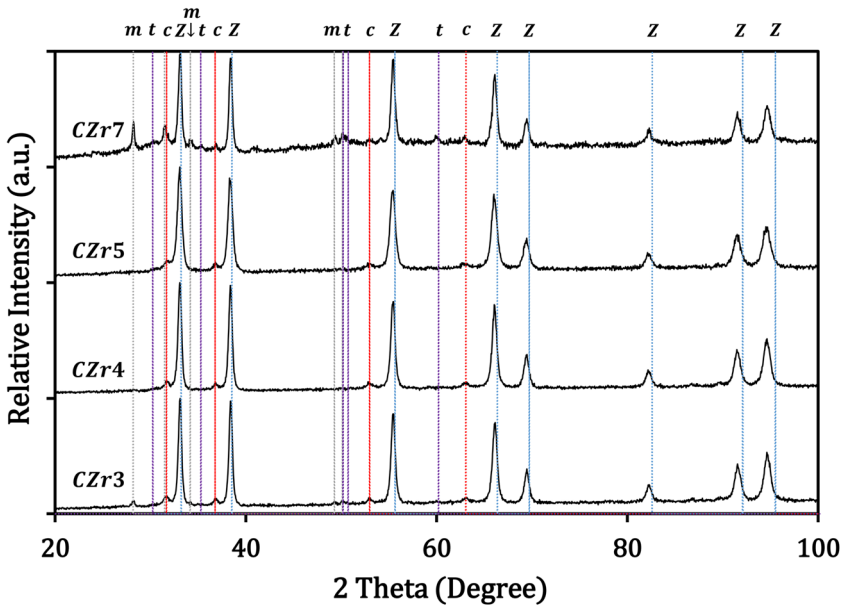

Fig. 7 XRD patterns of samples heated in vacuum at 1400 °C (c: c-ZrO_2, m: m-ZrO_2, t: t-ZrO_2, z: ZrC)

Since the amount of the carbide phase is linearly related to the area of the X-ray diffraction peaks, the area (A) beneath the (111) peak of the ZrC phase is calculated from Eq. (11) [19]. The percentage of ZrC phase in samples was calculated by dividing the area of all ZrC peaks to the total peak's area of each sample's XRD pattern according to Eq. (12).

$$A_{(hkl)} = \int_{2\theta_0}^{2\theta_f} I^{(hkl)}(2\theta)d2\theta \cong \sum_{n=0}^{n=f}\left(I_n^{(hkl)} - I_n^{0(hkl)}\right).\Delta 2\theta \qquad (11)$$

$$A_{Phase} = \sum_{n=1}^{n=n} A_n^{(hkl)}, \quad ZrC\ Phase\ (Volume\%) = \frac{A_{ZrC}}{A_{All\ phases}} \times 100 \qquad (12)$$

Figure 8 demonstrates the schematic method of the utilized phase content calculation. Table 2 shows the calculated carbide phase content of the CZr3, CZr4, CZr5, and CZr7 samples heated at 1400 °C in both vacuum and argon atmospheres. According to the quantitative phase analysis data, it is obvious that the amount of the carbide phase in the CZr4 sample is higher than the other ones after heating at 1400 °C in vacuum.

Figure 9 shows the crystallite size and lattice parameter values of ZrC phase of the samples heated at 1200 and 1400 °C under vacuum and argon which were calculated using the Scherrer formula according to Eq. (1), respectively [19]. As this figure shows, all heated samples at 1200 °C under argon flow have the lowest lattice parameters which represents the highest amount of oxygen dissolved in the carbide phase. In addition, heated samples at 1400 °C under argon flow have relatively more lattice parameters but still lower than all samples prepared under pyrovacuum condition at different temperatures.

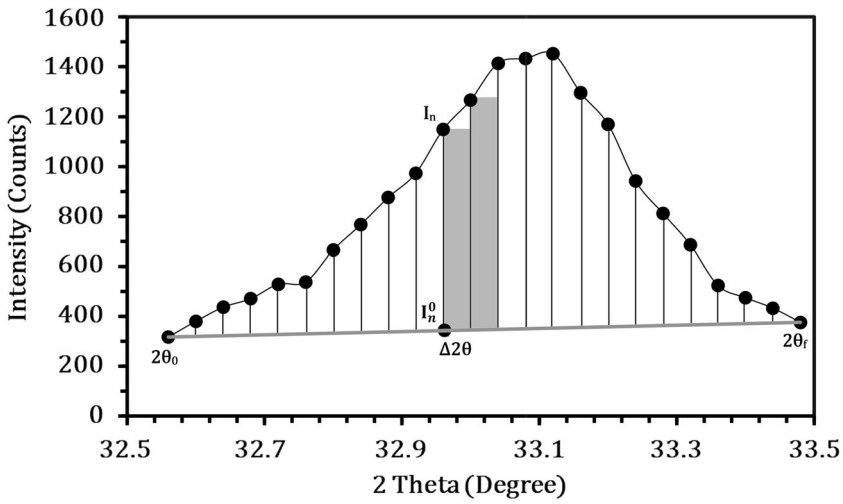

Fig. 8 Schematic method of the quantitative phase analysis of zirconium carbie

Table 2 Carbide phase content of samples heated at 1200 and1400 °C in vacuum and argon (vol.%)

Atmosphere	Argon	Argon	Vacuum	Vacuum
Temp. (°C)	1200	1400	1200	1400
CZr3	19.3	42.3	41.3	98.1
CZr4	16.9	54.6	57.68	99
CZr5	16.25	50.17	46.4	93.99
CZr7	7.5	35.7	37.2	60.9

The CZr4 sample has the largest crystallite size and lattice parameter values. After CZr4, by increasing the C/Zr molar ratio up to 7, both values of lattice parameter and crystallite size are decreased under pyrovacuum condition. According to Schönfeld et al. [30], the same phenomena of dependency of lattice parameter on carbon content has been reported. In the second step of the carbide phase formation, i.e., de-oxygenation of oxy-carbide phase, the lattice parameter increases. Chu et al. [31] report the carbothermal synthesis of ZrC nano-particles using zirconium nitrate and sucrose as starting materials. It is demonstrated that the formation of the round-shaped carbide grains with the particles size of 120–180 nm occurs at 1600 °C in argon atmosphere. However, the aggregation of particles is inevitable due to the high temperature of the applied heating regime. The lattice parameter of the obtained ZrC phase after heating at 1600 °C was also reported as 4.692 Å. Sacks et al. [32] reported the value of 4.696 Å for carbide phases heated at 1800 °C for 2 h in argon flow.

In two similar studies on the carbothermal reduction of ZrC, the lattice parameter values of 4.694 Å [12] and 4.697 Å [13] were reported. The differences between the experimental and theoretical (i.e., 4.702 Å [33]) values of lattice parameter are due to the varieties of the oxygen contents in the produced carbide phases in different methods. Gendre et al. [34] reported the lattice parameter value of 4.698 Å for the synthesized $ZrC_{0.97}O_{0.06}$ phase via a conventional carbothermal reduction using zirconia and carbon black after heating at 1750 °C for 8 h. Feng et al. [35] reported a value of 4.701 Å for the ZrC phase obtained from zirconia and phenolic resin as starting materials, after spark plasma sintering (SPS) at 1600 °C for 1.5 h. In the current research, the lattice parameter of the CZr4 sample heated under vacuum at 1400 °C for 3 h is calculated as equal to 4.7003 Å. To the knowledge of the authors, this is one the highest values among the available reports. According to EDS analysis of Fig. 10(b), it seems that due to the low oxygen content of the produced zirconium carbide phase the lattice parameter reached to this value [30]. By increasing the lattice parameter, the crystallite sizes of the samples would slightly increase.

Figure 10(a and b) shows the scanning electron microscopy images of the CZr4 sample, heated at 1200 °C and 1400 °C for 3 h under vacuum. In the microstructure of the sample heated at 1200 °C (Fig. 10(a)), according to the inserted EDS analysis, a matrix containing zirconia and carbon surrounding the ZrC particles can be observed. In the sample which was heated at 1400 °C, the matrix is converted to the smaller sized particles (Fig. 10(b)). The formation of polygonal shaped ZrC phase with particles size of less than 100 nm is clear in this micrograph according to the relevant EDS spectrum.

According to these results, it is believed that the formation of refractory zirconium carbide phase starts at less than 1200 °C under vacuum. Thermodynamic calculations reveal that under pyrovacuum condition, the decrease in Gibbs free energy due to the decrease in $P_{(CO)}$ leads to promotion of the carbothermal reaction. In addition, at 25% excess amount of carbon to zirconium molar ratio, the crystallite size and lattice parameter values of the zirconium carbide phase are increased. According to the literature, the lattice parameter and oxygen content of the carbide phase have a contrary relationship [35, 36].

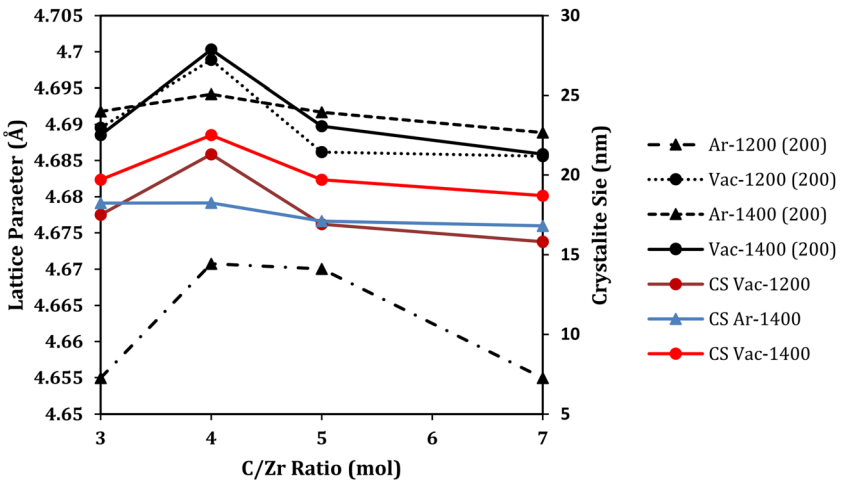

Fig. 9 The crystallite size and lattice parameter values of samples heated under argon and vacuum at 1200 and 1400 °C

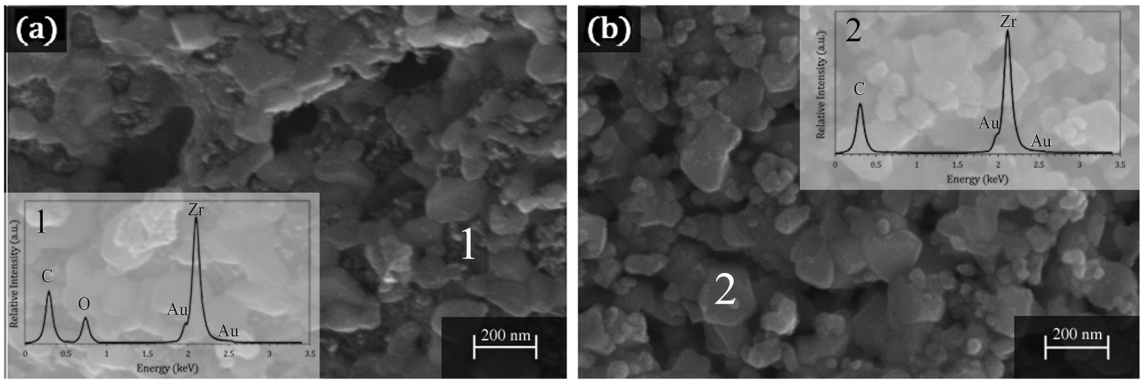

Fig. 10 SEM images and EDS spectra of CZr4 sample heated in vacuum at: (a) 1200 and (b) 1400 °C

Conclusions

In this research, the carbothermal reduction of zirconia is investigated and compared at different temperatures under vacuum and argon atmospheres. The thermogravimetric study of the stoichiometry sample (CZr3) in different atmospheres shows that the formation of carbide phase under vacuum condition starts at about 200 °C lower than that of argon condition. This fact was correctly predicted by the conducted thermodynamic calculations. It is proved that the reaction under pyrovacuum condition is more progressive rather than in argon atmosphere due to the higher obtained phase contents and lattice parameter values. The synthesized ZrC powder under vacuum at 1400 °C has the crystallite sizes smaller than 23 nm. The calculated lattice parameter values of the synthesized ZrC phase show that the oxygen content of the carbide phase produced under vacuum is much lower than those mentioned in the literature. The molar ratio of carbon to zirconium has a strong role in the ZrC synthesis and the optimized ratio has been determined to be equal to 4, which formed the highest carbide phase content (96.6 volume %) and lattice parameter (4.7003 Å). A microstructural analysis indicates the presence of polygonal-shaped particles of carbide phase smaller than 100 nm synthesized at 1400 °C under vacuum.

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