Perspective

A perspective to efficient synthesis of zirconium carbide via novel pyro-vacuum method: lower temperatures and enhanced purity

Faramarz Kazemi, Behzad Nayebi *

Department of Materials and Metallurgical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran

ABSTRACT

The use of ultra-high temperature ceramics (UHTCs) as a novel additive in the refractory industry is becoming increasingly popular. However, the synthesis of such materials is associated with some commercial obstacles, mainly high-temperature synthesis methods. In the present study, the pyro-vacuum method is presented as a new method to decrease the final product's synthesis temperature and oxygen content. Some thermodynamic aspects and phase evolution of the materials during the synthesis procedure are described for the synthesis of non-oxide material. Conclusively, it seems that by applying vacuum conditions, the final UHTC phases can be synthesized at significantly lower temperatures (>400 °C lower, for ZrC), if adequate powder mixtures are considered. Also due to phase analysis, it was found that the oxygen content of the final phase is lower than the conventional routes and other references. The process provides promising prospects for the economic synthesis of UHTCs.

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1. Introduction

Recently a wide range of carbide and boron-containing materials such as ZrC, ZrB_2, SiC, and TiB_2 as well as MAX phases such as Ti_3AlC_2 have been attended as hard refractory materials with outstanding properties such as high strength, thermal and electrical conductivity [1]. Similar to most of the refractory transition metal carbides (Table 1), ZrC is also widely researched recently, as a promising candidate for high-temperature applications due to its extreme melting point (over 3000 °C), solid phase stability and remarkable high-temperature thermomechanical behavior [2, 3].

Conventionally, such noble materials are synthesized at over 1600 °C under argon flow conditions [4–6]. Therefore, the commercialization of the mentioned process becomes an obstacle and the final price of these materials becomes extremely high, making it commercially challenging to add UHTCs in proper dosage or use them independently. However, the amount of remaining oxygen in the final products is always an obstacle and the nearest powder synthesized by conventional Argon methods was near 4.698 Å [7].

In the current study, the principles of pyro-vacuum method for synthesizing UHTCs are first introduced. Then, the thermodynamic principles of the pyro-vacuum method for the synthesis of UHTCs are presented with a focus on ZrC synthesis as a case study.

2. Pyro-vacuum's principles and theory

The pyro-vacuum process was invented for two different purposes: (I) to decrease the amount of dissolved gases such as oxygen and nitrogen in the molten metals (Eq. 1) and (II) to obtain the refractory metals by reaction between metal carbide and oxide phase at high temperatures and vacuum conditions (Eq. 2) [8]. Fig. 1 shows a schematic of the pyro-vacuum treatment of molten refractory metals.

$$[O]_M + M \rightarrow MO(g) \qquad (1)$$

Table 1. Common UHTCs and their properties.

Material	Crystal structure	Density (g/cm^3)	Melting point (°C)	Young's modulus (GPa)
HfC	FCC	12.76	3958	352
TaC	Cubic	14.50	3768	285
ZrC	FCC	6.56	3400	348
TiC	Cubic	4.94	3100	285
SiC	Polymorphic	3.21	2820	415
HfB$_2$	Hexagonal	11.19	3380	530
ZrB$_2$	Hexagonal	6.10	3245	500
TiB$_2$	Hexagonal	4.52	3225	551
TaB$_2$	Hexagonal	12.54	3040	257

$$MC + MO_x \rightarrow M + xCO(g) \tag{2}$$

For both of the above reactions, pressure can be increased by applying vacuum conditions at high temperatures, and purification or extraction of refractory metals can be achieved. Considering the term of Gibbs free energy (GFE) as Eq. 3, the relationship between temperature, pressure, and $[O]_M$ could be obtained through Eqs. 3 and 4.

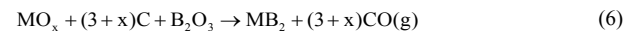$$\Delta G = \Delta G^0 + RT \ln K \tag{3}$$

in which, R refers to the universal gas constant, T shows the temperature, and K represents the equilibrium constant of the reaction (Eq. 2) and depends on a_0, the activity of oxygen in the metal:

Fig. 1. Schematic of pyro-vacuum process chamber.

$$P_{MO(g)} = a_0 . \exp\left(\frac{-\Delta G^0_{MO(g)}}{RT}\right) \tag{4}$$

In the synthesis of UHTCs, carbothermal reduction is the most feasible reaction. For carbides, carbothermal reduction is a common method according to Eq. 5:
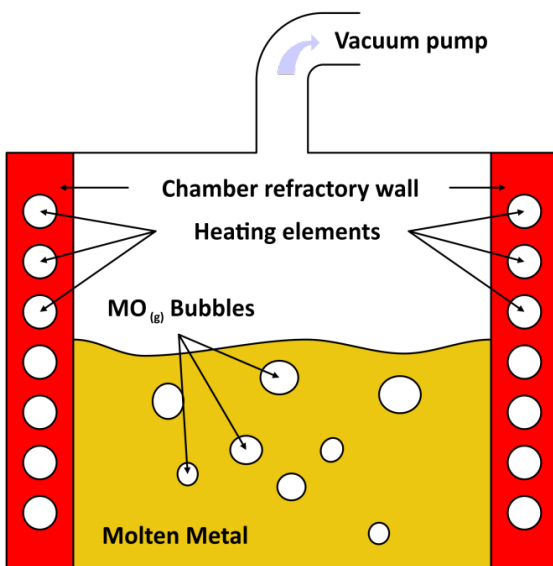
$$MO_x + (1+x)C \rightarrow MC + xCO(g) \tag{5}$$

However, for diboride phases, the carbothermal reduction reaction should be modified according to Eq. 6, as B_2O_3 is needed to provide boron:

$$MO_x + (3+x)C + B_2O_3 \rightarrow MB_2 + (3+x)CO(g) \tag{6}$$

It has been observed that these reactions are similar to those that occur during pyro-vacuum process. Therefore, it could be concluded that the use of this method could produce superior products compared to conventional methods. For example, due to the low temperature needed for the pyro-vacuum synthesis in comparison with conventional methods, the crystallite size of the product would be much smaller, which increases the mechanical properties of the final product. It also may provide better outcomes through a later sintering process in which, the low-angle boundaries (crystallite boundaries) may change to grain boundaries and inhibit common excessive grain growth. Potentially, pyro-vacuum synthesis can provide low oxygen content and remained carbon, if the stoichiometry of the synthesis reaction is controlled accurately.

The Gibbs free energy of the carbothermic reduction reaction (Eq. 5) for zirconia (ZrO_2) versus temperature at different partial pressures of CO gas (P_{co}) has been calculated and shown in Fig. 2 [9, 10]. According to Eq. 1, decreasing P_{co} at lower temperatures would result in diminishing the ΔG of the reaction ($\Delta G=0$). In other words, the equilibrium conditions of the reaction will take place. However, the mechanism of carbothermic reduction is much more complicated than Eqs. 5 and 6. Previous studies on the mechanism of carbothermal reduction under argon flow include two different approaches: thermal
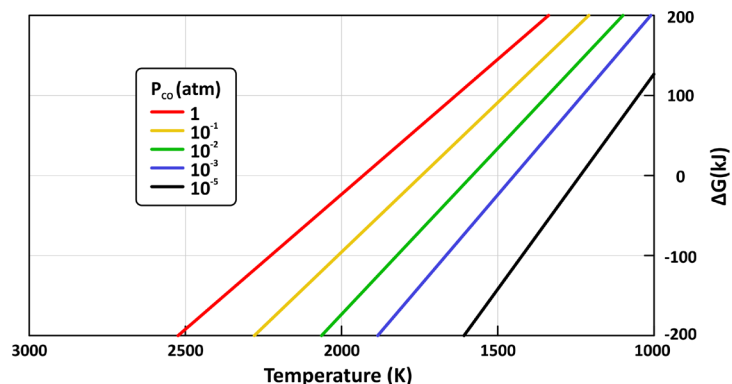
gravimetry [11] and microstructural evaluations [12]. While the former approaches have indicated a homogeneous solid-state reduction, the latter approaches confirm a 3-steps reaction. It has been reported that the first step includes zirconia reduction to ZrO and evaporation of the product (ZrO gas phase, Eq. 7). Then, the obtained ZrO gas reacts with CO generated from Eqs. 8 and 9, and results in the condensation of oxy-carbide phase through Eq. 10 (step 2). Finally, in the last step, the oxy-carbide phase can be further reduced by CO to form ZrC (Eq. 11) [13].

$$ZrO_2 \rightarrow ZrO(g) + \frac{1}{2}O_2(g) \tag{7}$$

$$C + \frac{1}{2}O_2(g) \rightarrow CO(g) \tag{8}$$

$$C + \frac{1}{2}CO_2(g) \rightarrow 2\,CO(g) \tag{9}$$

$$ZrO(g) + (3-3x)CO(g) \rightarrow ZrO_xC_{(1-x)} + (2-2x)CO_2(g) \tag{10}$$

$$ZrO_xC_{(1-x)} + 3xCO(g) \rightarrow ZrC + 2xCO_2(g) \tag{11}$$
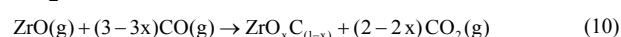
For a better comparison between pyro-vacuum and argon atmosphere, samples containing ZrO_2 and carbon with the preparation method described in Fig. 3 were heated at the same heating rate in an STA apparatus under argon flow (20 ml.min^{-1} flow rate) and vacuum
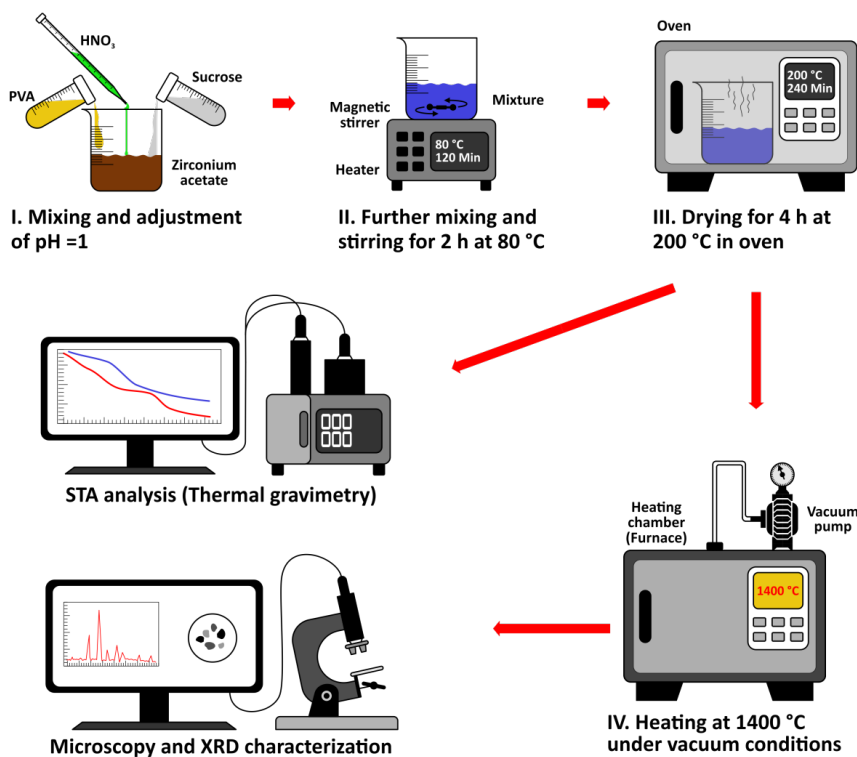

Fig. 3. Schematic of sample preparation and experimental procedure (inspired by Ref. [10] and drawn by the authors).
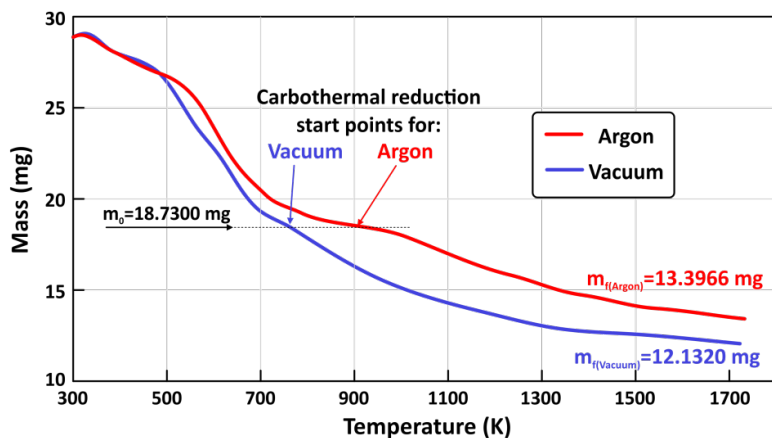
Fig. 4. Thermogravimetric (TG) analysis of precursors heated in argon and vacuum. "© Reproduced from Ref. [16] (J. Therm. Anal. Calorim.) with permission from Springer Nature Customer Service Centre. All rights reserved. The Licensed Material is not part of the governing OA license but has been reproduced with permission".

(10^{-6} mbar), respectively. This procedure for the synthesis of nanomaterials is very common [9, 10, 14–18] and many metal cations with different anion bases in association with different chelating agents could be used. The TG curves are shown in Fig. 4 and a decrease in the initial reduction temperature could be observed.

The results showed that the initial reduction temperature of calcined samples in argon and vacuum are 870 K and 740 K, respectively. These obtained results demonstrate that the carbothermal reduction of zirconia is a kind of heterogeneous reaction, due to the gas reaction provided by Eq. 10. More details about the interpretation of TGA analysis can be found in a previously published article [16].

Since the formation of the carbide phase nearly comes to an end at 1400 °C, the latter temperature is selected as the secondary condition. Fig. 5 shows the X-ray diffraction patterns of samples heated at 1200 °C and 1400 °C for 3 h in argon and vacuum conditions. As seen, the carbide content of samples heat-treated in a vacuum is extraordinarily higher than the one heated in argon at 1400 °C.

Fig. 6 shows the scanning electron microscope images of the sample heated at 1200 °C and 1400 °C for 3 h under vacuum. In the

microstructure of the sample heated at 1200 °C (Fig. 5a), according to the inserted EDS analysis, a matrix containing zirconia and carbon surrounding the ZrC particles can be observed. In the sample heated at 1400 °C, the matrix is transformed into smaller-sized particles (Fig. 5b). The formation of a polygonal ZrC phase with a particle size of less than 100 nm is visible in this micrograph according to the corresponding EDS spectrum.

The synthesized ZrC powder under vacuum at 1400 °C has a crystallite size smaller than 23 nm. Calculated lattice parameter values of the synthesized ZrC phase showed that the oxygen content of the oxy-carbide phase produced under vacuum is much lower than those mentioned before in the literature. Carbon to zirconium molar ratio plays an important role in the synthesis process of ZrC and the most optimized ratio was determined equal to 4 which led to the formation of the highest amount of carbide phase (99 wt%) and lattice parameter (4.701 Å). Microstructural analysis indicated the presence of polygonal-shaped particles of carbide phase smaller than 100 nm synthesized at 1400 °C under vacuum. Further discussion on XRD analysis is presented in the previously published articles [9, 10].
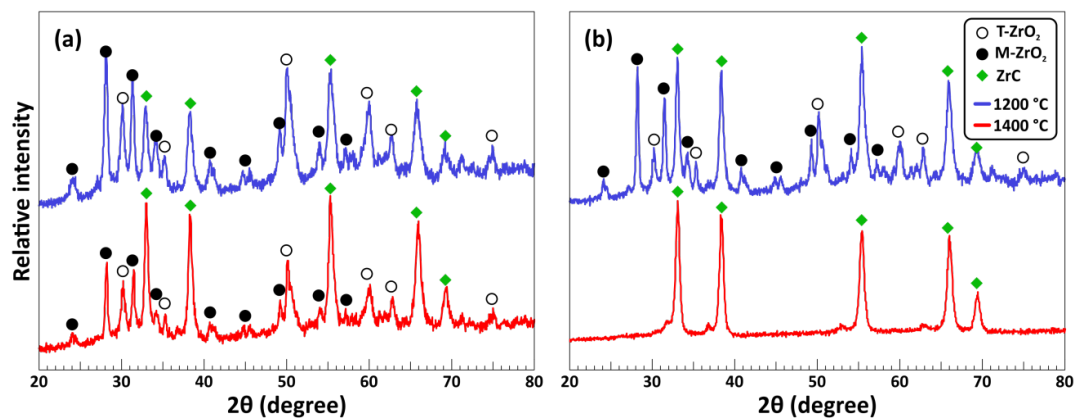

Fig. 5. XRD patterns of the samples heated at 1200 °C and 1400 °C for 3 h under a) argon and b) vacuum conditions. "© Reproduced from Ref. [16] (J. Therm. Anal. Calorim.) with permission from Springer Nature Customer Service Centre. All rights reserved. The Licensed Material is not part of the governing OA license but has been reproduced with permission".

Fig. 6. SEM images and EDS spectra of a sample heated in vacuum at a) 1200 and b) 1400 °C. "© Reproduced from Ref. [9] (J. Aust. Ceram. Soc.) with permission from Springer Nature Customer Service Centre. All rights reserved. The Licensed Material is not part of the governing OA license but has been reproduced with permission".
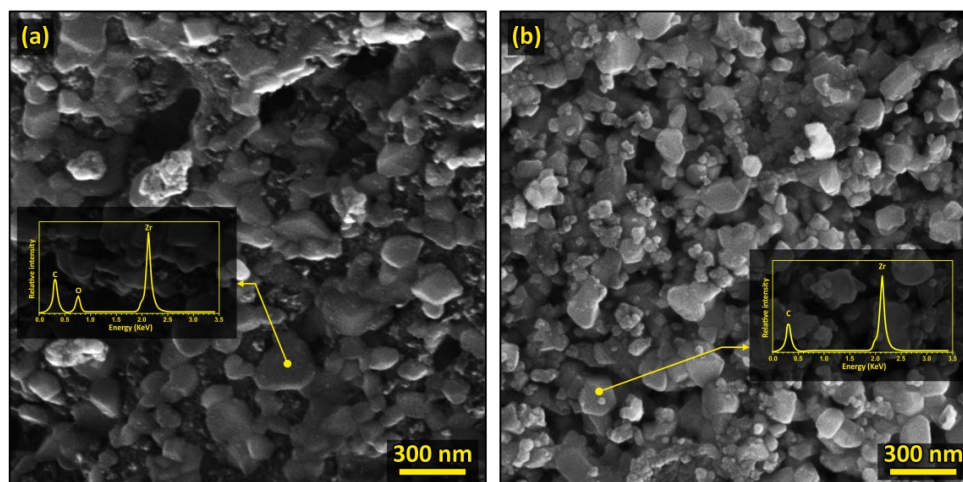
Nevertheless its thermodynamic, the pyro-vacuum methods should be also investigated kinetically, as the applied vacuum can be effective on the volatile and/or gaseous phases. Hence, while the process seems to be successful for transition metals with volatile low-capacity oxides such as Zr and Si, the method may not be applicable for other transition metals such as Nb, Ta, and Hf (with refractory and solid low-capacity oxides [8]).

3. Summary

As the results presented in previous research show, carbothermal reduction took place under pyro-vacuum conditions at much lower temperatures than under conventional conditions, making the process more feasible and commercialized.

This method resulted in nanoscale particles with particle sizes less than 100 nm, which is much more desirable for use as an additive in high-performance UHTCs. Hence, the process draws a promising perspective for the relatively low-temperature synthesis of fine UHTC powders with minimized impurities.

However, it should be considered that successful synthesis of the UHTCs via the pyro-vacuum method highly depends on the kinetic of the reactions, in addition to the thermodynamic aspects. Particularly, as many of the transition metals and elements provide refractory low-capacity oxides, the kinetic of the pyro-vacuum method may be so slow that the method could not result in high-purity products or fails in decreasing the synthesis temperature. Therefore, besides the theoretical investigations on the thermodynamic and kinetic of the pyro-vacuum method in the synthesis of UHTCs, experimental adjustment of the introduced method is essential and should be accurately researched.

CRediT authorship contribution statement

Faramarz Kazemi: Conceptualization, Methodology, Formal Analysis, Data curation, Investigation, Writing – original draft.
Behzad Nayebi: Validation, Writing – review & editing, Project administration, Supervision.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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