

SYNTHESIS AND CONSOLIDATION OF ZrC BASED CERAMICS: A REVIEW

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Abstract. Zirconium carbide is an extremely hard ultra high temperature ceramics (UHTC), used in nose cone, leading edge of rocket and supersonic vehicle, jet engines, fuel components of high temperature nuclear reactors, cutting tools, etc. Because of strong kinetic limitations of sintering like high covalent bonding, oxygen impurities on particle surface and low diffusion rate, both high temperature and external pressure are essential for consolidation of ZrC. Many researchers attempted various methods for sintering ZrC based systems. Addition of second phase, sintering additives and particle size and shapes can play significant roles in densification without deteriorating the high temperature desired properties. All the techniques for synthesis and consolidation of ZrC and its composites are reviewed.

1. INTRODUCTION

There are more than 100 materials available with melting temperatures over 2500 °C, including refractory metals (Hf, Re, Ta, W), oxides (HfO₂, UO₂, ThO₂), a variety of transition metal carbides, nitrides, and borides as well as other compounds. For UHTC applications, though, melting temperature is only one of many of properties used in the materials selection process. Other properties like mechanical strength (both room temperature and working temperature), thermal conductivity, thermal expansion, density, machinability, and, finally, cost are also important factors in determining the effective material for UHTC application. Most studies on UHTC focus on ZrB₂ based composites. However, it has relatively low eutectic temperatures with many adjoining structural materials like C-C and W based alloys (2390 and 2250 °C, respectively) and, hence, may not be suitable for very high temperature applications. Recently, there has been a restoration of sorts in materials originally studied in the last de-

cade for potential aerospace applications, driven by “the need for speed” - with new propulsion and hypersonics concepts where the propulsion combustion temperatures with solid propellants are typically in the range of 2200-3000 °C depending on propellant chemistry. For this reason, ZrC is one of the potential materials for high temperature applications in hypersonic vehicles and weapons points like re-entry vehicle, rocket/Scram jet engine or supersonic vehicle, several industrial sectors, such as foundry, nuclear power plants, cutting tools or metallurgical industries [1-15].

ZrC has a face centered cubic structure (rocksalt crystal structure) having Fm3m space group and lattice parameter is 4.6976 Å. Carbon is occupying the octahedral interstitial sites and a wide homogeneity region exists for the monocarbons. The complete stoichiometry is rarely formed in ZrC phase and the ratio of C to Zr can be varied from 0.3 to 0.98 [1]. It has potentially tailorable thermomechanical and thermophysical properties due to the large,

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substoichiometric phase stability field associated with vacancies in the C sublattice. Zirconium carbide (ZrC) ceramics have a high melting point (~3530 °C) due to strong covalent bonding of Zr-C (Enthalpy of formation $-197 \text{ kJ}\cdot\text{mol}^{-1}$); high hardness (~25 GPa), high electrical conductivity (resistivity $\sim 40 \mu\Omega\cdot\text{cm}$) due to presence of metallic Zr-Zr bond; high load bearing capabilities, excellent corrosion resistance against molten iron and slags, super thermal shock resistance. It has lower density ($6.73 \text{ g}/\text{cm}^3$) compared to other ultra high temperature ceramics (UHTC) based on carbides like WC, TiC, HfC etc.

2. SYNTHESIS OF ZrC BASED CERAMICS

For making phase pure and sinterable grade powder, the characteristics of precursor materials and processing routes are very crucial. The precursor materials' characteristics such as purity, particle size, morphology, defect concentration strongly stimulate the sinterability and defect induced ZrC_x phase. Moreover, selection of synthesis route and related processing parameters also play the key roles for making ZrC_x phase for specific applications. In this section, we discuss different routes for synthesis of ZrC based ceramics as follows: self-propagating high temperature (SHS) synthesis [1-6]; carbothermal reduction [11-16]; sol-gel processing from polymer and inorganic precursors [19-27]; chemical vapour deposition [36-44] and other advanced techniques.

2.1. From element(s) and metal halides

Self-propagating high-temperature synthesis (SHS) is a simple method for producing phase pure ceramic and intermetallic compounds by exothermic reactions in an area of a reactant mixture. The potential advantages of the SHS method is that the process requires less energy (only ignitor required) and shorter processing time, in seconds only. The temperature of the combustion can be very high (as 5000K) and the rate of wave propagation can be very rapid (as 25 cm/s). In addition, high temperature exothermic reactions expel volatile compounds and hence, yield high purity porous products. Since the last decade, many researcher have been using this process for producing transition metal boride and carbide compounds. M. Song et al. prepared ZrC by SHS process using ball milled Al, Zr, and C (nano size carbon black) powders as precursors. During reaction, ZrAl_3 metastable phase was formed and heat released by this reaction was utilised to synthesize ZrC particle [1]. The nonstoichiometric ZrC_x phase (x in the range from 0.3 to 0.98) can be tuned by controlling milling time of Zr powder [2]. These defects were created due to rapid thermal fluctuations (heating and cooling) during SHS and particle sizes of the product can be controlled by choosing metals. A. M. Nartowski et al. reported fast exothermic solid state metathesis reactions between CaC_2 and metal halides (i.e. ZrCl_4) for preparation of nano crystalline ZrC [6]. Table 1 summarizes the work related to synthesis of ZrC from its elements and halide.

Table 1. Synthesis of ZrC based ceramics.

Ref. #	Precursor	Process condition	Product quality
Section 2.1: From element(s)/metal halides			
1	Zr + C + Al	* Self-propagating high temperature synthesis (SHS) in argon (Ar) * 30-40 wt.% aluminium (Al) addition	* Without Al: ZrC particle size: $\sim 160 \text{ nm}$ * 30 wt.% Al: Spherical ZrC, particle size: $\sim 60 \text{ nm}$ * 40 wt.% Al: Tetragonal ZrC
2	Zr + C_7H_8	Mechanochemical activated synthesis (MAS) through ball milling at 400 rpm for 25 hrs in Ar	* Grain size $< 10 \text{ nm}$ (TEM), $\sim 7 \text{ nm}$ (XRD) * FCC crystal
3	Zr + C + Cu	* Combustion Synthesis (CS)/SHS in Ar * Without or 10-30 wt.% Copper (Cu)	* Irregular shaped $10 \mu\text{m}$ particles (without Cu) * Spherical shaped particles (up to 100 nm) (10-30 wt.% Cu)

4	Zr + C	Mechanical activation assisted (MA)-SHS in air	Homogeneous ZrC particle in micron range
5	Zr + Si + Phenolic resin	Pyrolysis at 1650 °C for 60 min	ZrC-SiC crystallite size < 400 nm
6	Zirconium halides + CaC ₂	Solid state metathesis in between 200 and 1000 °C for 2 days	Nanosized grain of ZrC powder

Section 2.2. Reduction synthesis

7	ZrO ₂ + C + Mg	SHS	* Particle size (avg): 320 nm * O ₂ : 3- 3.43 wt.%
8	ZrO ₂ + Mg + C + Fe	Combustion at 750 °C for 10 min in Ar	* ZrC-Fe * Particle size: 1-50 μm * Polygonal shaped
9	ZrO ₂ + Graphite	i. Ball milling for 24 hrs ii. Heat treatment at 1800 °C under 100 Pa in N ₂	* Graphitic layer encapsulated ZrC * Cubic NaCl Structure * Several hundred nm particle size
10	Zr powder + Pitch	Hot pressing at 2600 °C at 50 MPa	* ZrC/C composite * Low ablation rate (1×10 ⁻³ g/cm ² .s) at 15 wt.% Zr
11	ZrO ₂ + C	Carbothermal	ZrC
12	a. Polyzirconoxane + Phenolic resin b. ZrOCl ₂ .8H ₂ O + Phenolic resin	a. Solution based carbothermal at 1550 °C for 2 hrs in Ar b. Carbothermal at high temperature in Ar	a. * Particle size: 200-600 nm * Cubic crystal structure b. * Particle size: 200-600 nm * Nearly Cubic crystal
13	ZrOCl ₂ .8H ₂ O + Chitosan	Carbothermal at 1200-1550 °C for 2 hrs in Ar	Particle size: ~3 μm, O ₂ : ~3 at.%
14	ZrO ₂ + C	Carbothermal reduction a. At 1475 °C for 2 hrs in Ar b. At 1800 °C for 2 hrs in Ar	a. * FCC crystal * Crystallite size: ~100-130 nm * Lattice parameter: ~0.47 nm * O ₂ : 3.3 wt.%, C: 13.4 wt.% b. * Lattice parameter ~0.47 nm * O ₂ : 0.1 wt.%, C: 11.3 wt.%
15	ZrO ₂ colloid (5-10 nm) + Sucrose	Carbothermal at 1550 °C for 4 hrs in Ar a. C:Zr = 2 b. C:Zr = 4 c. Zr = 6	a. * Crystallite size: 106 nm * O ₂ : 5.1 wt.%, C: 19.1 wt.% b. * Crystallite size: 55 nm * O ₂ : 4.8 wt.%, C: 38.1 wt.% c. * Crystallite size: 41 nm * O ₂ : 3.5 wt.%, C: 57.1 wt.%
	ZrO ₂ powder (5-10 μm) + Sucrose	Carbothermal at 1550 °C for 4 hrs in Ar a. C:Zr = 2 b. C:Zr = 4 c. C:Zr = 6	a. * Crystallite size _{avg} : 150 nm * O ₂ : 4.81 wt.%, C: 11.62 wt.% b. * Crystallite size _{avg} : 115 nm * O ₂ : 6.1 wt.%, C: 32.6 wt.% c. * Crystallite size _{avg} : 103 nm * O ₂ : 2.9 wt.%, C: 37.8 wt.%

16	Zirconium acetate + Sucrose	Carbothermal at 1400 °C in vacuum	* Spherical shaped particles * Crystallite size < 20 nm
17	a. $ZrSiO_4 + 6C$ b. $ZrO_2 + SiO_2 + 6C_{amp}$	* Microwave-assisted Carbothermal reduction and carburization * 2.45 GHz Microwave irradiation at 700 W for 30 min in Ar * Longer processing time if N_2 is used instead of Ar	ZrC-SiC porous composites
18	$ZrCl_4 + C + NaHCO_3$	i. Ball Milling ii. Heating at 1200-1400 °C for 4 hrs in Ar	* ZrC particles * Crystallite size: ~ 150 nm
Section 2.3. Sol-gel route			
19	Zirconium n-propoxide + Furfuryl alcohol	Carbothermal reduction at 1450 °C	Crystallite size < 100 nm
20	Zirconium n-propoxide + CH_3COOH + Saccharose	a. Heating at 1400 °C for 3 hrs in Ar b. Heating at 1500 °C for 3 hrs in Ar c. Heating at 1600 °C for 3 hrs in Ar d. i. Heating at 1400 °C for 150 min in Ar ii. Heating at 1800 °C for 6 min in Ar	a. * Crystallite size: 93 nm * Lattice parameter: 4.690 Å * O_2 : 8 at.% b. * Crystallite size: 108 nm * Lattice parameter: 4.694 Å c. * Crystallite size: 150 nm * Lattice parameter 4.695 Å * O_2 : 3 at.% d. * Crystallite size: 110 nm * Lattice parameter: 4.697 Å
21	Zirconium n-propoxide + Pine wood + Acetic acid	Pyrolysis at 1600 °C for 1 hr in Ar	Porous ZrC/C composite
22	Titanium butoxide + Zirconium butoxide + Hydroquinol	Carbothermal reduction at 1500 °C in vacuum and Ar	ZrC - TiC
23	$Zr(OPr)_4$ + n-propanol + Acetic acid + Sucrose	Pulsed current heating up to 1700 °C in Ar a. C:Zr = 4 b. C:Zr = 4.2 c. C:Zr = 4.4 for 30 min d. C:Zr = 4.6	a. * $ZrC_{0.85}O_{0.12}$ * Lattice parameter: 4.688 Å * O_2 : 1.85 wt.% b. * $ZrC_{0.89}O_{0.09}$ * Lattice parameter: 4.690 Å * O_2 : 1.37 wt.% c. * $ZrC_{0.96}O_{0.04}$ * Grain size: 60-100 nm * Nearly spherical particles * Lattice parameter: 4.696 Å * O_2 : 0.64 wt.% d. * $ZrC_{0.97}O_{0.02}$ * Lattice parameter: 4.697 Å * O_2 : 0.32 wt.%
Section 2.4. Solution based method			
24	$ZrOCl_2 \cdot 8H_2O$ + Oxide bidentate ligands + Phenolic resin	Pyrolysis at 1550 °C for 2 hrs in Ar	* Crystallite size: 200-500 nm * Irregular polyhedron * O_2 : 2.5 at. %

25	Zirconium tetrakis (2,4-pentanedionate) + Phenolic resins	Heat treatment at 1100-1500 °C for 4 hrs in Ar	ZrC fibres
26	ZrOCl ₂ .8H ₂ O + Phenol + Paraformaldehyde + Acetylacetone	a. Pyrolysis at 1000 °C for 2 hrs in Ar b. Pyrolysis at 1500 °C for 2 hrs in Ar c. Pyrolysis at 1800 °C for 2 hrs in Ar	a. ZrC ₃₆ O ₉ b. ZrC ₃₃ O ₄ c. ZrC ₃₁ (highly crystalline)
27	Zr(OC ₄ H ₉) ₄ + Divinylbenzene	Pyrolysis at 1600 °C for 1 hr in Ar	Crystallite size: 106.4 nm

Section 2.5. From polymeric precursor

28	Cp ₂ Zr(CHCH ₂) ₂ + Borane (H ₃ B)	a. Pyrolysis at 1200 °C for 1 hr in Ar b. Pyrolysis at 1600 °C for 1 hr in Ar	a. * ZrC _{1.64} B _{0.59} O _{0.34} * O ₂ : 4.4 wt.% b. * ZrC _{1.30} B _{0.67} O _{0.01} * O ₂ : 0.19 wt.%
29	Cp ₂ Zr(CH=CH ₂) ₂ + Polymethylsilane (PMS)	a. Pyrolysis at 1400 °C for 1-2 hrs in Ar b. Pyrolysis at 1600 °C for 1-2 hrs in Ar c. Pyrolysis at 1800 °C for 1-2 hrs in Ar d. Pyrolysis at 2200 °C for 20 min in Ar	a. Grain size of β-SiC in ZrC-SiC composite: 2.77 nm b. Grain size of β-SiC in ZrC-SiC composite 5.82 nm, ZrC: 54.6 wt. % c. Grain size of β-SiC in ZrC-SiC composite: 20.94 nm d. Grain size of β-SiC in ZrC-SiC composite: up to 1 μm
30	ZrOCl ₂ .8H ₂ O Acetylacetone	a. Pyrolysis at 1200 °C for 2 hrs in Ar b. Pyrolysis at 1300 °C for 2 hrs in Ar c. Pyrolysis at 1400 °C for 2 hrs in Ar	a. * Crystallite size: 100-500 nm * O ₂ : 23.1 wt.% b. * Crystallite size: 20-100 nm (avg. 45 nm) * O ₂ : 8.4 wt.% c. * O ₂ : 3.9 wt.%
31	ZrC precursor + PCS	Pyrolysis at 1500 °C for 2 hrs in Ar	* ZrC-SiC composite * Uniform dispersion of SiC in ZrC * Crystallite size < 200 nm
32	Polyzirconoxane + Salicyl alcohol	Pyrolysis at 1300 °C in Ar	* Particle size: 50-100 nm * Cubic crystal
33	ZrC precursor + PCS	Liquid precursor conversion method	ZrC-SiC composite
34	ZrCl ₄ + n-C ₄ H ₉ Li	i. Colloidal precursor processing through reduction of ZrCl ₄ with n-C ₄ H ₉ Li in hexane ii. Heat treatment at 700-1000 °C for 2-12 hrs	* Cubic crystal * Crystal size: 7 nm
35	Zirconium acetate + Phenolic resin + Carbon fibre	i. Impregnation for 2 hrs ii. Carbonisation at 1000 °C for 30 min in N ₂ iii. 4 cycles of impregnation and carbonisation iv. Graphitization at 2000 °C C for 30 min	* ZrC-C/C composites * ZrC particle of submicron size

Section 2.6. Chemical Vapour Deposition (CVD)

36	$ZrCl_4 + C_xH_y$ ($x=1-3,$ $y=4,2,6$)	* At 1300-1600 °C * H_2 (0.024-0.3 m ³ /hr) as carrier * Ar (0-0.2 m ³ /hr) as diluents	* FCC crystal * Grain size: 2-5 μm * Growth rate: 150 nm/hr-50 μm/hr. * Presence of $ZrC_{0.7} + ZrC + C$
37	$ZrCl_4 + CH_4 + H_2$	* At 1150 °C-1400 °C for 2 hrs under 5 kPa; * Flow rates: $ZrCl_4$: 1.0 g/hr CH_4 : 10 ml/min H_2 : 40 ml/min Ar: 20 ml/min	* ZrC films * Star shape at 1200 °C * Columnar growth at 1300 °C * Cauliflower shape at 1400 °C
38	$ZrCl_4 + CH_4$	* At 1550±5 °C for 3 hrs under 5 kPa * Ar (carrier and diluent) * H_2 (reducing gas)	a. * Cubic crystal ZrC * Lattice parameter: 4.693 Å * Layer thickness : (100 ± 2) μm * $H_V^\#$: 25.3 ± 1.3 GPa * $Y^\#\#$: 312 ± 9 GPa at 300 mN * Strong (200) texture normal to substrate surface * ~5.5 mol.% minor phase b. $ZrC_{0.85}$ * Lattice parameter: 4.692 Å * H_V : 22.8 ± 1.3 GPa * Y : 302 ± 11 GPa at 300 mN, * ~5.5 mol.% minor phase
39	$ZrCl_4 + CH_4/C_3H_6 + H_2$	* At 1050-1400 °C under 50.66 kPa * H_2 (carrier and reductant) * Ar (diluent)	* Columnar growth at 1300 °C * Equiaxial growth at 1400 °C * Pyrolytic carbon like morphology
40	Methyl trichlorosilane + $ZrCl_4 + CH_4 + H_2$	At 800-1400 °C	Layer thickness: 800 nm at 1200 °C
41	$ZrCl_4 + C_3H_6 + H_2 + Ar$	Low pressure CVD at 850-1300 °C for 4-7 hrs	* Cubic crystal * Grain size: 20-30 nm * Layer thickness: 50 μm * $MAR^\#\#\#$: 0.11×10^{-3} g/s after ablation for 100 sec * $LAR^\#\#\#\#$: 0.36×10^{-3} mm/s after ablation for 100 sec
42	ZrC powder + C-fiber + Polydimethylsilane	* CVD and slurry over PIP-C/SiC * At 1100 °C for 5 hrs under 3 kPa	Exposure condition: * 30 sec in oxyacetylene flame * ~50% lower MAR of CVD layer than obtained for the substrate (0.0425 g/sec) * ~40% lower LAR of CVD layer than obtained for the substrate (0.0622 mm/s)
43	$ZrCl_4 + C_3H_6 + H_2$	* At 1050-1250 °C under 5.066 kPa * Ar (carrier gas)	* Loose spherical microstructure at 1050 °C * Cauliflower microstructure at 1150 °C * Glassy microstructure at 1250 °C

44	ZrCl ₄ + Carbon fibre (micro-coiled) + H ₂	Vapour Phase Metallising at 1100-1250 °C in Ar	<ul style="list-style-type: none"> * Coil shaped 10 nm ZrC grains at 1250 °C for 2 hr * 25% Zirconization at 1250 °C for 4 hrs * Bulk resistivity and BD^s was 10⁻¹S⁻¹·cm and 0.8 g/cc, respectively, for 2 hrs
Section 2.7. Infiltration			
45	Zirconium butoxide {Zr(OC ₄ H ₉) ₄ } + Divinylbenzene (DVB) + C	Precursor infiltration and pyrolysis (PIP) at 1200-1600 °C	<ul style="list-style-type: none"> * 3D-C/ZrC * $\sigma_f^{\$\$\$}$: 107.6 MPa * Y: 28.8 GPa * $K_{IC}^{\$\$\$}$: 7.03 MPa^m* BD: 1.98 g/cc * AP[@]: 12.4% * Actual matrix density: 4.38 g/cc * MAR: 0.012 g/s * LAR: -0.002 mm/s
46	PZC + PCS + Carbon fibre	<ul style="list-style-type: none"> i. 3:1 PZC:PCS infiltration in porous C-preform ii. Pyrolysis at 900 °C for 30 min iii. 4 times repetition of step i and ii for densification iv. Heat treatment at 1500 °C 	<ul style="list-style-type: none"> * 3D 4-directional C_f-C/ZrC-SiC * BD: 2.14 g/cc * AP: 10%, * σ_f: 474 MPa. * Under surface temperature 2127 °C for 600 sec * MAR: 0.01 g/s * LAR: 0.001 mm/s
47	PZC + PCS + C fiber	<ul style="list-style-type: none"> * Precursor infiltration and pyrolysis at 1500 °C, for 2 hrs in Ar * Ablation test at 3000 °C for 120 s in oxyacetylene flame 	<ul style="list-style-type: none"> * C/C-ZrC-SiC with ZrC: 12.20 vol.% and SiC: 16.38 vol.% * BD: 2.22 g/cc * AP: 19.7%, * σ_f: 128.37 MPa * LAR: 2.48×10⁻³ mm/s * MAR: -3.75×10⁻⁴ g/s
48	<ul style="list-style-type: none"> a. ZrC particle/PCS + C b. PZC/PCS + C 	<ul style="list-style-type: none"> Polymer infiltration and pyrolysis at 1500 °C for 90 min in Ar 	<ul style="list-style-type: none"> a. * 3D C_f/ZrC-SiC with ZrC: 14 vol.%, SiC: 7 vol.%, C fiber: 25 vol.% * Grain size : ~100 nm * BD: 2.06 g/cc * AP: 13% * σ_f: 308±35 N * Y: 106±4 GPa b. * 3D Cf/ZrC-SiC with ZrC: 25 vol.%, SiC: 11 vol.%, C fiber: 27 vol.% * Grain size: < 30nm * BD: 2.2 g/cc * AP: 8% * σ_f: 376±43 N * Y: 138±3 GPa
49	Zr containing polysilane	Precursor infiltration and pyrolysis at 2300 °C	<ul style="list-style-type: none"> * C/C-ZrC-SiC * BD: 1.69 g/cc * LAR: 0.00211 mm/s

50	a. PZC + C fiber cloth b. PZC + PCS + C fiber cloth	* Precursor infiltration and pyrolysis * Ablation test under oxidation at 1200 °C for 30 min	* MAR: 0.5179 mg/s a. * σ_f : 247.9 MPa * Y: 5.7 GPa * MAR: 30.6% b. * σ_f : 273.1 MPa * Y: 17.2 GPa * MAR: 20.1%
51	a. ZrC aqueous slurry + Highly branched polycarbosilane (HBPCS) + C b. ZrC precursor + HBPCS + C	CVI / Silicon infiltration / Polymer infiltration and pyrolysis at 1200-1800 °C in Ar	a. σ_f : 428±15 MPa b. * σ_f : 401±26 MPa
52	Zr + C	Reactive Melt Infiltration (RMI)	* Nano indentation hardness: 17.12±1.84 GPa * Micro indentation hardness: 12.05±1.77 GPa * Y: 258.97±17.75 GPa
53	Zr + C	RMI	C _f /ZrC
54	a. Zr ₂ Cu + Phenolic Resin b. Zr ₂ Cu + Asphalt	* RMI (in Vacuum) at 1200 °C for 1-3 hrs * Oxyacetylene (2066±14 °C for phenolic resin) * Oxyacetylene (2075±17 °C for Asphalt)	a. * σ_f : 285.4±9.7 MPa * Y: 76.2±4 GPa * K _{IC} : 8.9±0.8 MPam ^{1/2} * BD: 3.59±0.08 g/cc * AP: 4.3±0.5% * ZrC yield: 30.8 vol.% * MAR: 1.8±0.9 mg/s * LAR: 0.0011±0.0003 mm/s b. * σ_f : 224.8±7.2 MPa * Y: 48.1±3.5 * K _{IC} : 4.7±0.6 MPam ^{1/2} * BD: 3.84±0.05 g/cc * AP: 3.9±0.4 % * ZrC yield: 37.5±1 vol % * MAR: 0.8±0.3 mg/s * LAR: 0.0006±0.0002 mm/s
55	Zr + C	* RMI at 1850 °C in Ar * Ablation test under oxyacetylene torch and laser beam up to 3000 °C	* C/C-ZrC * LAR: 0.002±0.001 mm/s * MAR: 0.004±0.001 g/s
56	WC-PCS/DVB + Zr ₂ Cu	RMI at 1300 °C for 3 hrs in Ar	W-ZrC cermet
57	a. Zr ₇ Cu ₁₀ + C _f /C b. ZrCu + C _f /C c. Zr ₂ Cu + C _f /C	Liquid metal/vacuum infiltration at 1200 °C for 1-3 hrs under 0.5 Pa	a. * In the product ZrC: 27.9±1.7 vol.% * AP: 5.2±0.9 % * σ_f : 91.1±3.4 MPa * Y: 49.8±2.2 GPa * K _{IC} : 4.1±0.8 MPam ^{1/2} b. * In the product ZrC: 40.1±2.1 vol.% * AP: 5.5±0.7 % * σ_f : 98.2±3.1 MPa * Y: 43.5±2.8 GPa * K _{IC} : 5.5±0.5 MPam ^{1/2} c. * In the product ZrC: 43.7±2.8 vol.%

			* Porosity: 9.9±1.3 % * σ_f : 62.7±2.7 MPa * Y: 37.6±1.9 GPa * K_{IC} : 6.3±0.6 MPam ^{1/2}
58	Zr ₂ Si + Porous C _f /C perform	i. Porous C _f /C perform through CVI ii. RMI of Zr ₂ Si in porous perform at 1800 °C under 0.08 Pa followed by Ar purging	* C/C-ZrC * BD: 2.46 g/cc * AP: 5 % * LAR: 0.028 mm/s * σ_f : 239.5 MPa
59	C fiber + ZrC powder + Si + SiC (by CVD)	Vapour Silicon Infiltration at 1700 °C for 1.5 hrs under 1 Pa	a. * C _f /ZrC-SiC without any interface * ZrC:26 vol.%, fiber: 28 vol.% * BD: 2.01 g/cc * AP:10% * σ_f : 121 ±13 MPa * Y: 17±2.0 GPa b. * C _f /ZrC-SiC with PyC/SiC interface * ZrC:24 vol.%, fiber:25 vol.% * BD: 2.25 g/cc * AP: 6% * σ_f : 301 ±15 MPa * Y: 25±4.0 GPa
60	ZrOCl ₂ .8H ₂ O + Natural wood Wood source: a. Oak b. Cherry c. Lime d. Beech	Vacuum Infiltration and Pyrolysis at 1550 °C for 1 hr in Ar	ZrC wt.% a. by XRD: 55.8±0.3 by FTIR: 59.4±1.5 b. by XRD: 62.6±0.3 by FTIR: 64.2±8.6 c. by XRD: 51.4±0.3 by FTIR: 59.3±1.7 d. by XRD: 74.7±0.3 by FTIR: 78.5±6.9
61	a. Zr ₂ Cu + C b. ZrCu + C c. Zr ₇ Cu ₁₀ + C	Vacuum Infiltration at 1200 °C for 3 hrs	C _f /ZrC with a. * ZrC: 43.7±2.8 vol.% * AP: 9.9±1.3 % b. * ZrC: 40.1±2.1 vol.% * AP: 5.5±0.7 % c. * ZrC: 27.9±1.7 vol.% * AP: 5.2±0.9 %
62	Zr ₂ Cu + C	a. Vacuum Infiltration at 1200 °C for 2 hrs b. i. Vacuum Infiltration, 1200 °C for 2 hrs ii. Heat treated at 1800 °C for 2 hrs in vacuum	a. * C _f /ZrC with ZrC: 43.8±2.1 vol.% * AP: 6.9±1.2 % * σ_f : 120.4±2.8 MPa * Y: 68.7±3.3 GPa * K_{IC} : 6.9±0.5 MPam ^{1/2} b. * Cf/ZrC with ZrC:45.2±1.8 vol.% * AP: 12.7±1.6 % * σ_f : 104.7±3.2 MPa * Y: 58.8±1.9 GPa * K_{IC} : 8.7±0.7 MPam ^{1/2}

63	Zr ₂ Cu + WC	Displacive compensation of porosity (DCP) method at 1200-1300 °C under ambient pressure	* RD ^{@@} : 96.5% AP: 3.5% for 52% porous WC * RD: 94.4% AP: 5.6% for 44.6% porous WC * Thermal shock resistance under solid fueled Pi-K test
64	Zr ₂ Cu + WC	DCP at 1150-1300 °C under ambient pressure	* ZrC-W composite * RD: 94- 99.9%
65	C + PZC + PCS	Mold Pressing & Polymer infiltration and pyrolysis at 900 °C	a. * ZrC: 34 vol.%, Fiber: 34 vol.% * BD: 2.26 g/cc * AP: 7.2.% * σ_f : 143±21MPa * Y: 89±33GPa b. * ZrC: 31 vol.%, Fiber: 45 vol.% * BD: 2.17 g/cc * AP: 8.3% * σ_f : 343±26MPa * Y: 153±9GPa c. * ZrC: 25 vol.%, Fiber: 56 Vol.% * BD: 2.13 g/cc * AP: 6.9% * σ_f : 582±80MPa * Y: 167±25GPa

Section 2.8. Other advanced technique

66	(mixture of K ₂ ZrF ₆ , KCl, NaCl) + C	Molten salt reaction at 800-1000 °C	Coating thickness: 2 µm at 900 °C for 5 hrs
67	Polymer precursor containing Zr and Si	* Salt metathesis reaction * Pyrolysis at 1400 °C	* ZrC/SiC composite * Crystalline size: 100-200 nm
68	ZrCl ₄ + C	i. Microwave-Hydrothermal process, ii. Graphitisation at 2500 °C for 2 hrs in Ar	* C/C-ZrC * BD: 1.78 g/cc * Graphitization degree: 76.7%
69	Polycrystalline ZrC target (Plasmaterials, Inc.)	* Pulsed laser deposition, * Atmosphere of CH ₄ (2 × 10 ⁻³ Pa) * No of pulse: 30,000 * Substrate temperature: a. 30 °C b. 300 °C	a. * Grain size: 6.1 nm * Y: 240±10 GPa * nano H: 20±1 GPa * micro-strain: 2% * BD: 5.80 g/cc * RMS Surface roughness: 0.8 nm * Critical angle: 0.678° b. * Grain size: 12.3 nm * Y: 291±13 GPa * nano H: 41±2 GPa * micro-strain: 1.7% * BD: 6.10 g/cc

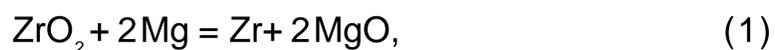
		c. 500 °C	<ul style="list-style-type: none"> * RMS Surface roughness: 1.1 nm * Critical angle: 0.698° c. * Grain size: 19.4 nm * Y: 320 ± 17 GPa * nano hardness: 48 ± 3 GPa * micro-strain: 1.6% * BD: 6.6 g/cc * RMS Surface roughness: 1.3 nm * Critical angle: 0.723°
70	Zr + Ethanol	Pulsed Plasma in Liquid (PPL) <ul style="list-style-type: none"> * Low voltage AC * Pulse * Single pulse duration: 3 μs * Frequency: 60 Hz * Current: ~20 A * Cathode vibration * Frequency: 5000 vibrations per min 	<ul style="list-style-type: none"> * ZrC covered with graphitic window * Particle size of ZrC: 10 nm * Morphology: FCC crystal
71	Zr + Ethanol	Pulsed Plasma in Liquid (PPL)	Particle size: 10 nm
72	ZrCl ₄ + CH ₄	RF Atm Pressure Plasma synthesis process <ul style="list-style-type: none"> * Ar (Carrier) * H₂ (to increase conversion rate) 	<ul style="list-style-type: none"> * Particle size <100 nm * Surface area: 36.56 m²/g
73	Zr + CH ₄	Reactive Plasma Process <ul style="list-style-type: none"> * 20 MeV electron beam irradiation of 9×10¹³–3.6×10¹⁴ cm⁻² * CH₄ and H₂ at a ratio of 5:2 	ZrC
74	Zr(OC ₄ H ₉) ₄ + C ₂ H ₄	Laser Pyrolysis <ul style="list-style-type: none"> * Ethylene sensitizer * Ar flow (between 250-2000 sccm) * C₂H₄ flow (between 800-1600 sccm) * Then annealing for 1 hrs in Ar for O₂ removal 	Grain size: 38 nm
75	Zr, Al, Ni, Cu, ZrC	High pressure gas atomization	ZrC/Zr ₅₅ Al ₁₀ Ni ₅ Cu ₃₀
76	Zirconium acetyl acetate + Phenolic resins	Electrospinning (and annealing) <ol style="list-style-type: none"> i. Electrospinning <ul style="list-style-type: none"> * at + 26 kV * with a mass flow rate of 1.0 mL/h * and a working distance of 10 cm * mixture of ethyl alcohol and 2,4-pentanedione as solvent * H₂SO₄ ii. Annealing at 800-1600 °C for 2 hrs in Ar 	<ul style="list-style-type: none"> * ZrC nano fiber * ZrC phase started to form at 1500 °C for 2 hrs in Ar
77	ZrC target	Sputtering <ul style="list-style-type: none"> * D. C. magnetron sputtering * 150 W d.c. power 	* Thickness: 150-200 nm (for 6 min deposit time)

		* Base pressure of the deposition chamber: 3×10^{-6} Torr	
		* Working pressure during deposition: 8×10^{-3} Torr	
		* Ar (carrier gas) for a total flux of 50 sccm	
		* Si substrate	
		* Deposition time: 6 min	
		* Growth temperature:	* Grain size of
		a. 25 °C	a. 7.2 nm
		b. 180 °C	b. 12.1 nm
		c. 290 °C	c. 3 .5 nm
78	ZrSiO ₄ + Graphite	Pack cementation	* ZrC-SiC multi coating * SiC-rich inner layer and * ZrC out layer
79	Zr + Si + PCS + 3D C/SiC	Pack cementation	* ZrC-Zr ₂ Si coating * Thickness: 10 mm by controlling infiltration composition
80	Zr + C	* Gas evaporation method (smoke experiment) * Ar gas, Heating	* 5 nm crystallites of ZrC grain * NaCl type structure (though external shape became spherical)

#: H_V/H = Vicker hardness/Hardness, ##: Y = Young modulus, ###: Mass ablation/loss rate, ####: Linear ablation/recession rate, \$: BD = Bulk density, \$\$: σ_f : Flexural strength/Bending strength, \$\$\$: K_{IC} = Fracture toughness, @: AP = Apparent (open) porosity, @@: RD: Relative Density.

2.2. Reduction synthesis

Carbothermal reduction is a common chemical process for synthesis of different non-oxide powders like ZrC, ZrB₂, TiC, etc. under various conditions [7-18]. The preparation of different carbides has been studied since the last two decades. The reduction of different precursors like ZrO₂, zirconium oxy-chloride, zirconium silicate, zirconium acetate, etc. was generally used. The first stage of reaction was associated with a considerable temperature rise due to highly exothermic oxidation reaction of metal like aluminum, magnesium. The next stage was marked by moderate temperature rise of the system due to the mild exothermic reaction of ZrC formation. The most common method for synthesis of ZrC is as follows:



The adiabatic temperature of the reaction of ZrO₂-C-Mg system reaches approximately 2000K that is much higher than the melting point (923K) of Mg metal. The process results in some loss of carbon which generates non-stoichiometric carbide. J. Li et al. prepared nanosized ZrC powder (~320 nm) by SHS process by exothermic reduction reaction of ZrO₂-C-Mg. After completion of the reaction, the re-

action product consists of ZrC and MgO and finally Mg was leached out by acid wash [7]. Another way to increase the reactivity of the green powders is the process that combines simultaneous ball milling and an SHS reaction. J. Dong *et al.* prepared encapsulated ZrC with graphite layers by high energy ball milling of carbon with ZrO₂ ball and subsequent heat treatment at 1800 °C under N₂ gas atmosphere [9]. The reactivity of carbothermal reduction through gas phase diffusion transport leads to pronounced change in burning wave velocity, temperature, product shape, and reactants-to products conversion efficiency [13-16]. M. D. Sacks et al. also produced nanosized ZrC powder by reduction of ZrO₂ with carbon in argon atmosphere at 1800 °C with less oxygen impurity (0.1 wt.%) [14]. Recently, many efforts have been made to accelerate carbothermal reduction reactions and simplify the synthesis process using microwave irradiation. B. P. Das et al. prepared porous composite via microwave-assisted carbothermal reduction and carburization process under argon atmosphere [17]. Table 1 summarizes the reported works on synthesis of ZrC by carbothermal reduction process [7-18].

2.3. Sol-gel route

An alternative processing route for ZrC synthesis is sol-gel route. In this wet chemical route, the mixing

of precursors is at finer level than conventional routes and synthesis can be possible at relatively lower temperature. The main advantages of this route are that the reactants are distributed homogeneously at molecular level and hence, reduce the kinetic barriers between metal oxide/alkoxide and carbonaceous precursor. C. Ang et al. prepared nanocrystalline (~100 nm) ZrC via sol-gel route by using zirconium n-propoxide and furfuryl alcohol as precursor. A block copolymer P123 surfactant was used for intimate mixing. Formation of ZrC started at 1250 °C and full conversion took place at 1450 °C [19]. The main requirement of polymer precursor is that it is stable and processable up to its decomposition temperature. M. Dolle et al. synthesized nanosized (~90-150 nm) zirconium carbide by sol-gel method using zirconium n-propoxide, acetic acid, and saccharose as precursor materials and then pyrolysis in argon atmosphere to convert them into nanosized tetragonal zirconia and reactive amorphous carbon. Finally, further heat treatments between 1400 to 1800 °C for 3 h of these precursors converted into nanosized zirconium carbide [20]. J. Xie et al. synthesized ZrC (60-100 nm) by combination of sol-gel and pulsed current heating. Zirconium n-propoxide, n-propanol, acetic acid, and sucrose were taken as starting materials for preparing zirconia with carbon. Then pulsed current heating at 1750 °C for 30 min (heating rate of 100 °C/min) in argon atmosphere under 65 MPa was carried out [23].

2.4. Solution based method

The name solution based process is a generalized term for low temperature synthesis chemical routes which involves solution of the desired or gelation of a droplet of sol. *Solution based* methods are intended at eliminating powder handling and the problems associated with it. However, very few reports are available on synthesis of metal carbides via solution route. C. Yan et al. prepared nanosized ZrC (200-500 nm) by solution based processing of zirconium oxychloride octahydrate, oxide bidentate ligands (acetylacetone, lactic acid, ethylene glycol, salicylic acid) and phenolic resin as carbon source. $ZrOCl_2 \cdot 8H_2O$ and oxide bidentate ligands were used to prepare zirconium-containing complexes and then pyrolysed at 1400-1550 °C with phenolic resin in flowing argon at a heating rate of 8 °C/min with 2 h soaking [24]. I. Hasegawa et al. prepared ZrC fibres by solution sol gel process from zirconium tetrakis (2,4-pentanedionate) and novolac-type phenolic resins as raw materials followed by heating at 1100-1500 °C for 4 h in argon [25]. D. Zhao et al. prepared

ZrC by precursor infiltration of zirconium butoxide and divinylbenzene and then pyrolysis upto 1600 °C in argon for 1 h at a heating rate of 10 °C/min [27].

2.5. From polymeric precursor

The liquid polymer precursor method can be processed advantageously because of its liquid state mixing that forms well distributed homogeneous microstructure and promoted the mechanical and chemical properties. The advantages of polymer precursors are that they are stable, easy to handle, and contain stoichiometric amount Zr and C. H. Wang et al. prepared ZrC/ZrB₂ composite from preceramic polymer precursor (PZCB) by reaction between $Cp_2Zr(CH=CH_2)_2$ and borane. The PZCB precursor was finally pyrolysed in the range of 1200-2200 °C under argon and formed ZrC-ZrB₂ composite [28]. X. Tao et al. prepared nanosized (20-100 nm) spherical shaped ZrC from pyrolyzing of polyzirconoxanesal at 1200-1400 °C for 2 h in argon atmosphere [30]. X. Tao et al. prepared cubic ZrC (50-100 nm) by using polyzirconoxane (PZO) and salicyl alcohol followed by pyrolysis at 1300 °C [32].

2.6. Chemical vapour deposition (CVD)

Chemical vapour deposition is a special process used to prepare high purity, oxygen free thin coatings (ZrC, SiC, ZrB₂, etc). However, for producing hard ZrC coating, deposition parameters such as gas flow, thermodynamics and molar ratio of the precursors, carbon source effect, deposition temperature, reactant pressure and nature of substrate and its position, etc [36-44]. It is well reported that the ZrC phase exists when the molar ratio of zirconium to carbon varies in the range of 1:1 to 1:0.61. The non-stoichiometry phases of ZrC may affect the structural and chemical properties of ZrC coating. S. Wei et al. prepared ZrC films on graphite substrates by chemical vapour deposition process using $ZrCl_4$ at 1300-1600 °C, where CH_4 , C_2H_2 , and C_3H_6 were used as carbon source and hydrogen and argon were used as carrier gas and dilution gas respectively [36]. Y. Long et al. deposited ZrC and ZrC_{0.85} coating on graphite substrate by CVD by using $ZrCl_4$, CH_4 , argon, H_2 at 1550±5 °C for 3 h under 5000±5 Pa pressure. It was found that the mechanical properties of non-stoichiometry ZrC_{0.85} coating was lower in comparison with stoichiometric ZrC [38]. Low pressure chemical vapour deposition (LPCVD) can only be performed at high temperatures, reduces the rate of the reaction and reduces

thickness variations. It also improves the coating's purity and internal structure. S.-L. Wang et al. prepared ZrC coating (~50 mm thick and grain size ~20-30 nm) by LP-CVD process on 2-D C/C specimen by using $ZrCl_4$ in C_3H_6 , H_2 , Ar gas atmosphere at 850-1300 °C for 4-7 h [41]. S. Motojima et al. prepared micro-coiled ZrC fibres by vapour phase metalizing of micro-coiled carbon fibres using $ZrCl_4$, carbon fibre (microcoiled) in H_2 and Ar gas mixture at 1100-1250 °C. Table 1 gives the comparative summary of CVD synthesis of ZrC [44].

2.7. Infiltration

Compared with conventional hot pressing and chemical vapour deposition technique, infiltration method is a novel method for fabrication of complex shaped and large scale production at relatively lower temperature. The researchers tried different infiltration routes into 3D/2D preform for making ZrC/C composites like polymer infiltration, metal infiltration in both liquid and vapour phases. Polymer infiltration and pyrolysis (PIP) is the method of fabrication of ceramic matrix composites comprising an infiltration of a low viscosity preceramic polymer or sol into the reinforcing ceramic structure (e.g. 3D porous fabric, fibre) followed by pyrolysis and finally it decomposes and converts into a ceramic. D. Zhao et al. prepared ZrC composite in 3D carbon matrix by precursor infiltration and pyrolysis at 1600 °C by using mixture of zirconium butoxide and divinylbenzene as precursor of ZrC [45]. Q. Li et al. fabricated 3D 4-directional Cf/ZrC–SiC composites by PIP method with PZC (ZrC precursor) and PCS (SiC precursor) impregnation. Precursor mixture was then infiltrated into the carbon fiber preform and finally pyrolysis and densification were carried out at 900 °C and 1500 °C, respectively [46]. Q. Li et al. fabricated two different kinds of 3D needled Cf/ZrC–SiC composites by ZrC particles/ polycarbosilane preceramic polymer and Zr-containing polymeric precursor (PZC)/ polycarbosilane separately and infiltrate into the carbon fiber preform followed by curing and pyrolysis at 900 °C for 30 min. Moreover, it was heated at 1500 °C for 90 min under argon atmosphere for better crystallinity. It was found that 3D Cf/ZrC–SiC composite with PZC/PCS showed good anti-ablation properties [48]. The metal infiltration method (RMI) is one of the novel infiltration methods that has several variations, including using a dispersion of ZrC particulate/alloy slurry to infiltrate into the 2D/3D preform, or using chemical vapour deposition to coat carbon on the ZrC powders/fibers, followed with infiltrating liquid Zr to re-

act with the carbon to form ZrC. With these methods, chemical reactivity, melt viscosity, and wetting between two components should be considered carefully. L. Zou et al. prepared C fiber reinforced ZrC matrix composites Cf/ZrC via RMI by infiltrating C fiber preform with Zr melt [52,53]. S. Wang et al. prepared 3D C/ZrC at 1200 °C by vacuum infiltrating porous C/C preforms with molten Zr_2Cu alloy. Zr_2Cu alloy was heated up to 1200 °C in vacuum and porous C/C preform were dipped into the melt for 1-3 h and finally cooled [54]. Y. Tong et al. prepared excellent ablation resistant C/C–ZrC composite by chemical vapor infiltration combined with Zr_2Si alloyed reactive melt infiltration at 1800 °C for 30 min [58]. Q. Li et al. prepared 3D-needled Cf/ZrC–SiC by vapour silicon infiltration at 1700 °C for 1.5 h under 1 Pa pressure. The composite exhibited non-brittle fracture behaviour and excellent high temperature properties due to formation of $ZrSiO_4$ [59]. M. M. L. Guerrero et al. prepared ZrC-based biomorphic ceramics by vacuum infiltration of $ZrOCl_2 \cdot 8H_2O$ sol into natural wood followed by pyrolysis at 800 °C for 1 h under argon atmosphere. Finally the products were pyrolysed at 1550 °C for 1 h under Ar atmosphere [60]. Y. Zhu et al. fabricated Cf/ZrC at 1200 °C for 3 h by vacuum infiltrating Cf/C preform with Zr_7Cu_{10} , ZrCu, and Zr_2Cu alloy [61-62]. Table 1 gives the comparative summary of different infiltration synthesis of ZrC based composites [45-65].

2.8. Other advanced techniques

Analyzing ZrC based literature, it becomes clear that the above mentioned processes are very efficient and common for the reactions and fabrication of ZrC based composites. However, other limited sophisticated techniques are also tried by few groups like molten salt reaction, microwave hydrothermal synthesis, pulse laser deposition/pyrolysis, electrospinning, etc. to synthesize fine ZrC ceramics or thin coatings [66-80]. S. Chen et al. prepared ZrC coating on C/C composite via molten salt reaction at 800-1000 °C by using molten salt mixture of KCl, NaCl, and K_2ZrF_6 as a reactive medium. Here K_2ZrF_6 transported Zr from the molten salt to C/C composite surface [66]. C. Li et al. prepared highly conductive C/C–ZrC composites by microwave-hydrothermal reaction of $ZrCl_4$ and carbon fibre felt followed by densification and graphitization at 2500 °C for 2 h in argon [68]. V. Craciun et al. prepared very hard nanocrystalline ZrC films on Si (100) substrate by pulsed laser deposition technique from a polycrystalline ZrC target at temperature of 30-500 °C under highly pure CH_4 [69]. L. Chen et al. synthe-

sized encapsulated nanocrystalline (10 nm) ZrC in graphitic carbon by pulsed plasma in liquid method, where zirconium electrode and ethanol were used as sources of Zr and carbon, respectively, and samples exhibited good anti-oxidation properties [70]. L. Bai et al. synthesized ultrafine ZrC powder (<100 nm) via radio frequency atmospheric-pressure plasma process by using $ZrCl_4$ and CH_4 as precursor and this process is effective for large scale processing [72]. X. M. Cui et al. fabricated ZrC nanofibre by electrospinning and annealing at 1400-1600 °C by using a solution of zirconium acetyl acetonate, phenolic resins dissolving in a solvent mixture of ethyl alcohol and 2,4-pentanedione [76]. Table 1 gives the comparative summary of different advanced synthesis of ZrC based composites [66-80].

3. CONSOLIDATION OF ZrC CERAMIC

Densification of the group IV transition metal carbides like ZrC is extremely difficult due to its strong covalent bonding and low self-diffusion rate. Moreover, oxygen and moisture present in ZrC powder surface (depleted amount of surface oxygen) acts as boundary phase that hinder the diffusion process

(sintering) and also promote grain growth of the system. In general, to overcome these difficulties, ZrC and its composites have been densified typically by pressure-assisted sintering, e.g., hot pressing, hot isostatic pressing, spark plasma sintering at above 1800 °C. The sintering process is taking place by surface diffusion and evaporation-condensation mechanism at relatively lower temperature and grain boundary and volume diffusion at higher temperature. The abnormal grain growth can occur at longer soaking at high temperature which restricts the densification and hence, results poor structural properties. Many researchers tried to sinter ZrC monolithic and its composites in different ways at relatively lower temperature and pressure. We are categorising these methods in two different sectors: i) using additive that forms thermodynamically reactive liquid phase during pressureless sintering; ii) using pressure assisted solid state sintering by conventional sintering process or field assisted sintering.

Moreover, a few groups of researchers also tried other advanced routes like laser processing for surface densification of porous ZrC. Different consolidation techniques are tabulated in Table 2.

Table 2. Composition and processing parameters of consolidation.

Ref #	Composition	Processing parameters	RD and some Properties
Section 3.1. Reactive and pressureless sintering			
81	a. Zr + C b. Zr + C c. Zr + C d. Zr + 0.8C e. Zr + 0.8C f. Zr + 0.67C g. Zr+0.5C	Post heat treatment at 1800 °C for 1 h (after RHP for 30 min under 40 MPa in vacuum at a. 1200 °C b. 1400 °C c. 1600 °C d. 1200 °C e. 1400 °C f. 1200 °C g.1200 °C	a. RD : 77%, Impurity: Zr, C b. RD: 83% c. RD: 85% d. RD: 92% e. RD: 96% f. RD: 98%, Grain size: 3.6 ± 3.3 μm g. RD: 99%, Grain size: 9.1 ± 4.5 μm
82	a. ZrC + 5 wt.% Si	* 1600 °C, * 40 MPa pressure from 1350 °C * vacuum atm (<10 Pa) below 1000 °C * and Ar atm after 1000 °C * soaking for 2 hrs	a. * $ZrC_{0.8}$ -13.4 vol.% SiC * (+trace ZrSi) by XRD * ZrC-10 vol.% SiC-2.6 vol.% ZrSi by Image * RD: 98% * $H_{V1.0}$: 20.5 ± 1.0 GPa * K_{IC} : 3.30 ± 0.1 MPa $\text{m}^{1/2}$ * 3 point bending strength: 819 ± 102 MPa

	b. ZrC + 10 wt.% Si		<p>b. * $ZrC_{0.8}$-16.7 vol.% SiC 10.9 vol.% ZrSi by XRD</p> <p>* ZrC-14.5 vol.% SiC-13.2 vol.% ZrSi by Image</p> <p>* RD: 98%</p> <p>* $H_{V1.0}$: 19.0 ± 0.5 Gpa</p> <p>* K_{IC}: 2.9 ± 0.3 MPa m^{1/2}</p>
83	ZrC + TiC	Reactive sintering at 1900 °C	<p>* ZrC-TiC composite</p> <p>* H: 20 GPa</p> <p>* K_{IC}: ~ 7 MPa m^{1/2},</p> <p>* ZrC (80 wt.%)-TiC (20 wt.%) had highest K_{IC} value compared to other ratio</p>
84	<p>a. ZrC</p> <p>b. ZrC (95 vol.%) MoSi₂ (5 vol.%)</p> <p>c. ZrC (90 vol.%) + MoSi₂ (10 vol.%)</p> <p>d. ZrC (80 vol.%) + MoSi₂ (20 vol.%)</p>	Sintering at 1950 °C for 60 min in Ar	<p>a. RD: $\sim 73\%$</p> <p>b. RD: 83.4%</p> <p>c. RD: 92.7%</p> <p>d. * RD: 96.8%</p> <p>* H_V: 12.7 GPa</p> <p>* K_{IC}: 3.5 MPa m^{1/2}</p> <p>* Y: 346 GPa</p> <p>* σ_f: ~ 272 MPa at RT</p> <p>* 156 MPa at 1200 °C</p>
85	<p>a. ZrC (80 vol.%) + Mo (20 vol.%)</p> <p>b. ZrC (70 vol.%) + Mo (30 vol.%)</p> <p>c. ZrC (60 vol.%) + Mo (40 vol.%)</p>	Sintering at 2150 °C for 60 min in H ₂ /He	<p>a. * Y: 380 GPa</p> <p>* σ_f: 320 MPa</p> <p>* Pore: 2.8% (SEM)</p> <p>b. Pore: 2.4% (SEM)</p> <p>c. * Y: 365GPa</p> <p>* σ_f: 410 MPa</p> <p>* Pore: 2.3% (SEM)</p>
86	<p>a. ZrC + Mo (20 vol.%)</p> <p>b. ZrC + Mo (30 vol.%)</p> <p>c. ZrC + Mo (40 vol.%)</p>	Sintering at 2150 °C for 60 min under 0.067 MPa in He/5% H ₂	<p>a. * BD: 6.87 g/cc</p> <p>* Total porosity: 2.8 %</p> <p>* σ_f: 324 MPa</p> <p>* Y: 380 GPa</p> <p>* Poisson's ratio: 0.20</p> <p>b. * BD: 7.05 g/cc</p> <p>* Total Porosity: 2.4%</p> <p>* σ_f: 343 MPa</p> <p>* K_{IC}: 2.64 MPa m^{1/2}</p> <p>* Y: 375 GPa</p> <p>* Poisson's ratio 0.21</p> <p>c. * BD: 7.68 g/cc</p> <p>* Total porosity: 2.2%</p> <p>* σ_f: 406 MPa</p> <p>* Y: 365 GPa</p> <p>* Poisson's ratio 0.23</p>
87	ZrC + MoSi ₂ (20 vol.%)	Sintering at 1927 °C for 60 min in Ar	RD: 95%
88	ZrC + MoSi ₂ (20 vol.%)	Sintering at 1950 °C for 60 min	RD: 94.67%

Section 3.2. Hot pressing (HP)

89	a. ZrC monolithic b. ZrC monolithic c. ZrC + VC (1 vol.%) d. ZrC + VC (2.5 vol.%) e. ZrC + VC (10 vol.%) f. ZrC + NbC (10 vol.%) g. ZrC + TaC (10 vol.%)	60 min under 30 MPa in Ar at a. 1900 °C b. 2000 °C c. 1900 °C d. 1900 °C e. 900 °C f. 2000 °C g. 2000 °C	a. RD: 80% b. RD: 92% c. RD:86%, $Zr_{0.985}V_{0.015}C$ d. RD:98%, $Zr_{0.982}V_{0.018}C$ e. RD:98%, $Zr_{0.982}V_{0.018}C$ f. RD:95.1%, $Zr_{0.896}Nb_{0.104}C$ g. RD:90.7%, $Zr_{0.895}V_{0.105}C$
90	ZrC (85 vol.%) + TaSi ₂ (15 vol.%)	Sintering at 1697 °C for 6 min under 30 MPa in vacuum	* RD: 99.9% * H_V : 17.9 GPa * K_{IC} : 3.6 MPa m ^{1/2} * σ_f : 503 MPa
91	ZrC (30 vol%) + W (70 vol%)	Sintering at 2200°C for 120 min under 25 Mpa	ZrC/W composite
92	a. ZrC (95 vol.%) + MoSi ₂ (5 vol.%) b. ZrC (90 vol.%) + MoSi ₂ (10 vol.%) c. ZrC (85 vol.%) + MoSi ₂ (15 vol.%)	Sintering at 1900 °C for 60 min under 30 MPa	a. * H_V : 22.8 ± 0.1 GPa * K_{IC} : 2.6 ± 0.1 MPa m ^{1/2} b. * H_V : 21.8 ± 0.1 GPa * K_{IC} : 3.2 ± 0.1 MPa m ^{1/2} c. * H_V : 20.7 ± 0.1 GPa * K_{IC} : 3.6 ± 0.1 MPa m ^{1/2}
93	ZrC + SiC (30 vol.%)	Sintering at 2000 °C for 60 min in Ar	RD: 98.4%
94	ZrC + SiC (20 vol.%)	Sintering at 2000 °C for 60 min under 30 MPa	RD: 97%
95	ZrC (2.11 mm)	Sintering at 1900 °C under 50 MPa	* RD: 99% * H_V : ~17.5 GPa at 10N load * γ : 415 GPa * Shear Modulus:172 GPa * Bulk Modulus: 234 GPa * Poisson ratio: 0.205
96	ZrC + YSZ (40 wt.%)	Sintering at 2000 °C for 60 min	* RD: ~99.9 % * K_{IC} : 5.8 MPa m ^{1/2} * σ_f : (4 pt bending): 320 MPa
97	ZrC (80 vol.%) + SiC _w (20 vol.%)	Sintering at 1900 °C for 60 min under 30 MPa	* RD: 99.2 % * K_{IC} : 5.03 MPa m ^{1/2} * σ_f : 626.17 MPa

Section 3.3. Spark plasma sintering (SPS)

98	ZrC	75 MPa at	
	a. Without milling (~3 mm)	a. 2100 °C	a. RD: ~98%
	b. Ball mill, 1 min (~450 nm)	b. 2100 °C	b. RD: ~99%
	c. Ball mill, 3 min (~175 nm)	c. 2055 °C	c. RD: ~99.9%
	d. Ball mill, 5 min (~130 nm)	d. 2030 °C	d. RD: ~99.9%
	e. Ball mill, 10 min (~65 nm)	e. 2000 °C	e. RD: ~99.9%
	f. Ball mill, 30 min (~30 nm)	f. 1890 °C	f. RD: ~99%
	g. Ball mill, 60 min (~20 nm)	g. 1900 °C	g. RD: ~99.9%
	h. Ball mill,180 min (~10 nm)	h. 1850 °C	h. RD: ~99.9%

99	a. ZrC monolithic	Sintering at 1950 °C for 15 min under 50 MPa in vacuum	a. * RD: 87% * Y: 252 GPa
	b. ZrC (90 wt.%) + SiC (10 wt.%)		b. * RD: 100% * Y: 410 GPa
	c. ZrC (70 wt.%) + SiC (30 wt.%)		c. * RD: 97% *Y: 424 GPa
100		Sintering at	
	a. ZrC (~3 μm) + SiC (~0.55 μm) (5 vol.%), without milling	a. ~2100 °C	a. RD: ~ 98.5%
	b. ZrC + SiC (5 vol.%), ball milled 1 min (~530 nm)	b. ~2100 °C	b. RD: ~99.9 %
	c. ZrC + SiC (5 vol.%), ball milled 3 min (~220 nm)	c. ~2055 °C	c. RD: ~99.9%
	d. ZrC + SiC (5 vol.%), ball milled 5 min (~170 nm)	d. ~2045 °C	d. RD: ~99.9%
	e. ZrC + SiC (5 vol.%), ball milled 10 min (~85 nm)	e. ~1990 °C	e. RD: ~99.9%
	f. ZrC + SiC (5 vol.%), ball milled 30 min (~31 nm)	f. ~1995 °C	f. RD: ~99.9%
	g. ZrC + SiC (5 vol.%), ball milled 60 min (~19.9 nm)	g. ~1900 °C	g. RD: ~99.9%
	h. ZrC + SiC (5 vol.%), ball milled 180 min (~12 nm)	h. ~1840 °C	h. RD: ~99.9%
	i. ZrC(~3 μm) + SiC(~0.55 μm) (17.5 vol.%), without milling	i.~2030 °C	i. RD: ~99.3%
	j. ZrC + SiC (17.5 vol.%), ball milled 1min (~600 nm)	j. ~1998 °C	j. RD: ~99.9%
	k. ZrC + SiC (17.5 vol.%), ball milled 3 min (~235 nm)	k. ~1980 °C	k. RD: ~99.9%
	l. ZrC + SiC (17.5 vol.%), ball milled 5 min (~180 nm)	l. ~1998 °C	l. RD: ~99.9%
	m. ZrC + SiC (17.5 vol.%), ball milled 10 min (~90 nm)	m. ~1950 °C	m. RD: ~99.9%
	n. ZrC + SiC (17.5 vol.%), ball milled 30 min (~37 nm)	n. ~1930 °C	n. RD: ~99.9%
	o. ZrC + SiC (17.5 vol.%), ball milled 60 min (~24 nm)	o. ~1895 °C	o. RD: ~99.9%
	p. ZrC + SiC (17.5 vol.%), ball milled 180 min (~13.8 nm)	p. ~1880 °C	p. RD: ~99.9%
	q. ZrC(~3 μm) + SiC(~0.55 μm) (30 vol. %), without milling	q. ~2102 °C	q. RD: ~99.2%
	r. ZrC + SiC (30 vol.%), ball milled 1 min (~700 nm)	r. ~2078 °C	r. RD: ~99.9%
	s. ZrC + SiC (30 vol.%), ball milled 3 min (~300 nm)	s. ~2000 °C	s. RD: ~99.9%
	t. ZrC + SiC (30 vol.%), ball milled 5 min (~230 nm)	t. ~2028 °C	t. RD: ~99.9%
	u. ZrC + SiC (30 vol.%), ball milled 10 min (~104 nm)	u. ~1983 °C	u. RD: ~99.9%

	v. ZrC + SiC (30 vol.%), ball milled 30 min (~41 nm)	v. ~1995 °C	v. RD: ~99.9%
	w. ZrC + SiC (30 vol.%), ball milled 60 min (~28 nm)	w. ~1995 °C	w. RD: ~99.9%
	x. ZrC + SiC (30 vol.%), ball milled 180 min (~15 nm)	x. 1900 °C	x. ~99.9%
101		3 min under 75 MPa at	
	a. ZrC	a. 2100 °C	a. *RD: 99% * H_V : 17.9 GPa
	b. ZrC + MoSi ₂ (1 vol.%)	b. 1950 °C	b. * RD: 99% * H_V : 18.8 GPa • K_{IC} : 2.1 MPa m ^{1/2}
	c. ZrC + MoSi ₂ (3 vol.%)	c. 1900 °C	c. *RD: 99% * H_V : 18.4 GPa * K_{IC} : 3.2 MPa m ^{1/2}
	d. ZrC + MoSi ₂ (9 vol. %)	d. 1700 °C	d. * RD: 99% * H_V : 20.0 GPa * K_{IC} : 3.3 MPa m ^{1/2}
102		Sintering at 1950 °C for 2 min under 50 MPa in Ar	
	a. ZrC (33.3 mol.%) + ZrB ₂ (33.3 mol.%) + SiC (33.3 mol. %)		a. * RD: 98.7% * H_V : 19.1 GPa * K_{IC} : 6.1 MPa m ^{1/2} * Y: 477 GPa
	b. ZrC (15 mol. %) + ZrB ₂ (70 mol.%) + SiC (15 mol.%)		b. * RD: 98.5% * H_V : 21.5 GPa * K_{IC} : 6.0 MPa m ^{1/2} * Y: 517 GPa
	c. ZrC(70 mol.%) + ZrB ₂ (15 mol.%) + SiC (15 mol.%)		c. * RD: 98.5% * H_V : 19.5 GPa * K_{IC} : 4.6 MPa m ^{1/2} * Y: 435 GPa
	d. ZrC(55 mol.%) + ZrB ₂ (15 mol.%) + SiC (30 mol.%)		d. * RD: 99.1% * H_V : 18.8 GPa * K_{IC} : 5.5 Mpa m ^{1/2} * Y: 449 GPa
	e. ZrC(20 mol.%) + ZrB ₂ (30 mol.%) + SiC (50 mol.%)		e. * RD: 98.6% * H_V : 20.4 GPa * Y: 486 GPa
	f. ZrC(15 mol.%) + ZrB ₂ (55 mol.%) + SiC (30 mol.%)		f. * RD: 98.7% * H_V : 19.6 GPa * K_{IC} : 5.7 Mpa m ^{1/2} * Y: 500
	g. ZrC(30 mol.%) + ZrB ₂ (55 mol.%) + SiC (15 mol.%)		g. * RD: 98.8% * H_V : 19.4 GPa * K_{IC} : 5.0 Mpa m ^{1/2} * Y: 496 GPa
	h. ZrC(55 mol.%) + ZrB ₂ (30 mol.%) + SiC (15 mol. %)		h. * RD: 98.5% * H_V : 19.6 GPa * K_{IC} : 5.6 Mpa m ^{1/2} * Y: 457 GPa GPa
103		Sintering at 1950 °C	
	a. ZrC _x monolithic	a1) 10 min 40 MPa a2) 5 min 100 MPa a3) 10min 100 MPa	a1) RD: ~91.7% a2) RD: ~95.7% a3) RD: ~96.5%

	b. ZrC_x (89 mol.%) + ZrB_2 (11 mol.%)	b1) 5 min 100 MPa b2) 10 min 100 MPa	b1) RD: ~98% b2) RD: ~98%
	c. ZrC_x (73 mol.%) + ZrB_2 (27 mol.%)	c1) 5 min 100 MPa c2) 10 min 100 MPa	c1) RD: ~97.5% c2) RD: ~97.9%
	d. ZrC_x (43 mol.%) + ZrB_2 (57 mol.%)	d1) 5 min 100 MPa d2) 10 min 100 MPa	d1) RD: ~97.1% d2) RD: ~97.5%
104	ZrC	Sintering at 2000 °C for 5 min under 50 MPa	RD: 96%
105	Zr + C	Sintering at 1245 °C for 30 min under 10 MPa, 6 V, negligible current	ZrC layer of thickness: 10-15 μ m
106	a. Commercial powder compact of $ZrB_2/ZrC = 1:1$ molar ratio b. Mixing powder compact of Zr:B:C = 2:2:1 molar ratio c. MA-powder compact of Zr:B:C = 2:2:1 molar ratio d. MA-SHS powder compact of Zr:B:C = 2:2:1 molar ratio e. MA-SHS powder compact of Zr:B:C = 4:2:3 molar ratio f. MA-SHS powder compact of Zr:B:C = 3:2:2 molar ratio g. MA-SHS powder compact of Zr:B:C = 3:4:1 molar ratio h. MA-SHS powder compact of Zr:B:C = 4:6:1 molar ratio i. MA-SHS powder compact of Zr:B:C = 5:8:1 molar ratio	Sintering at 1800 °C for 5-10 min under 40 MPa	a. *RD: 97.6% *H: 16.6 GPa * K_{IC} : 3.4 Mpa m ^{1/2} b. *RD: 96.9% *H: 13.7 GPa * K_{IC} : 3.8 Mpa m ^{1/2} c. *RD: 97.2% *H: 13.8 GPa * K_{IC} : 4.5 MPa m ^{1/2} d. *RD: 98.5% *H: 17.8 GPa * K_{IC} : 3.8 MPa m ^{1/2} e. *RD: 97.6% *H: 17.5 GPa * K_{IC} : 3.0 MPa m ^{1/2} f. *RD: 98.8% *H: 17.4 GPa * K_{IC} : 2.9 MPa m ^{1/2} g. *RD: 98.2% *H: 14.4 GPa * K_{IC} : 4.8 MPa m ^{1/2} h. *RD: 98.4% *H: 14.5 GPa * K_{IC} : 5.1 MPa m ^{1/2} i. *RD: 97.5% *H: 13.6 GPa * K_{IC} : 4.2 MPa m ^{1/2}
107	$ZrC_{0.96}$	a. Sintering at 2000 °C for 6 min under 70 MPa b. Sintering at 2100 °C for 30 min under 40 MPa	a. BD: 6.59 g/cc b. BD: 6.61 g/cc

3.1. Reactive and pressureless sintering

Pressureless sintering is a simple and economic sintering method of a powder compact especially at high temperature, depending on composition and particle size of the precursor powders. In general, the *pressureless sintering* process is performed by green compaction followed by sintering at temperature under ambient or controlled atmosphere. For some non oxide materials, the pressureless sinter-

ing process is carried out by addition of liquid forming additives like Y_2O_3 , Al_2O_3 , $MoSi_2$, $TaSi_2$, Mo, Ni etc.

C. Nachiappan et al. obtained nonstoichiometric ZrC_x ($x=0.5$ to 1) by reactive hot pressing from Zr and graphite with various molar ratio at 1200-1600 °C at 40 MPa [81]. The maximum density (99%) of the product obtained at low temperature i.e. 1200 °C. X.-G. Wang et al. prepared ZrC-SiC composites by reactive hot pressing using ZrC and Si (0-10 wt.% addition) at up to 1600 °C for 2 h under 40 MPa

pressure. During heat treatment above 1300 °C, ZrC reacted with Si to form ZrSi and SiC and for further heating at high temperature (1600 °C) carbon from remaining ZrC diffused into the ZrSi to form ZrC_{1-x} and SiC composite [82]. L. Silvestroni et al. consolidated ZrC by PLS at 1950 °C for 60 min under Ar atmosphere (~1 atm) with addition of 5-20 vol.% MoSi₂. Composite pellet to be sintered were prepared by cold isostatic pressing under 350 MPa pressure. Monolithic ZrC showed ~ 73% relative density, which increased with increasing of MoSi₂ content and reached 96.8% relative density at 20 vol.% MoSi₂ [84]. L. Charpentier et al. consolidated ZrC-MoSi₂ composite via PLS at 1927 °C for 60 min under Ar by adding 20 vol.% MoSi₂ resulting 95% relative density [87]. L. Silvestroni et al. consolidated ZrC-MoSi₂ composite by PLS/Liquid Phase Sintering at 1950 °C for 60 min with 20 vol.% addition of MoSi₂ resulting 94.67% relative density [88].

3.2. Hot pressing (HP)

Hot pressing technique is a high-pressure powder compaction process of high performance materials at a temperature high. This technology is mainly used for the manufacturing of various hard and covalent materials which are difficult to sinter via liquid phase processing or pressure less sintering. X-G. Wang et al. consolidated ZrC with VC, NbC, and TaC as additive via hot pressing at 1900-2000 °C for 1 h. VC was the optimum additive because of its limited solid solution (solubility limit=1.3 vol.% at 1900 °C) which resulted 98% density with 2.5 vol.% VC addition at 1900 °C [89]. L. Silvestroni et al. consolidated ZrC-15 vol.% TaSi₂ composites via hot pressing at 1697 °C for 6 min at 30 MPa pressure under vacuum resulting 99.9% densified composites [90]. The composite was O₂ resistant upto 1527 °C and until first 10 min of 1727 °C. T. Zhang et al. consolidated ZrC(30 vol.%)-W(70 vol.%) via hot pressing at 2200 °C for 2 h under 25 MPa pressure resulting 98% density [91]. B. N-Gonzalez et al. consolidated ZrC-MoSi₂ via hot pressing at 1900 °C for 1 h at 30 MPa pressure [92]. J. Li et al. consolidated ZrC- 20 vol.% SiC_{whisker} by hot pressing at 1900 °C for 60 min at 30 MPa pressure resulting 99.2% density. Flexural strength and fracture toughness were 626.17 MPa and 5.03 MPa m^{1/2}, respectively [97].

3.3. Spark-plasma-sintering (SPS)

Spark plasma sintering (SPS), also known as field assisted sintering technique (FAST) or pulsed electric current sintering (PECS), is an advanced sin-

tering technique which takes only a few minutes to complete a whole sintering process compared to other conventional sintering which may take hours or even days for the same. The main advantages of SPS are that it can confine the unwanted sintering reactions in case of highly reactive systems due to high heating rate and less holding time. B. N-Gonzalez et al. consolidated additive free ZrC by SPS at various temperature under 75 MPa pressure. Crystallite (feed) size effect was thoroughly studied, which was governed by high energy ball milling time [98]. D. Pizon et al. consolidated ZrC-SiC composite via SPS at 1950 °C for 15 min in vacuum under 50 MPa pressure, where heating rate was 100 °C/min upto 1900 °C and then at a rate of 50 °C/min to 1950 °C. ZrC-SiC 30 wt.% had oxidation resistance upto 1527 °C and, on the other hand, ZrC-SiC 10 wt.% showed better behaviour at higher temperature (1727 °C) [99]. F. Goutier et al. consolidated ZrC_x-ZrB₂ via SPS at 1950 °C for 10 min at 100 MPa pressure under vacuum. ZrB₂ lead to better densification. Shrinkage temperature (1620 °C for ZrC_x) shifted towards 1430 °C when ZrB₂ was 57 mol.% [103]. D.D. Jayaseelan et al. consolidated ZrC via SPS at 2000 °C for 5 min under 50 MPa resulting in 96% density. The product contained < 1% pore and average grain size was ~10 nm [104]. Heather F. Jackson et al. consolidated ZrC_{0.96} via SPS at 1900-2180 °C for 6-30 min under 40-70 MPa pressure resulting in 96-99% relative density [107].

4. CONCLUDING REMARKS

The densification of group IV transition metal carbides like ZrC is extremely difficult due to its strong covalent bonding between Zr-C and low self-diffusion rate. For better densification some tailoring should be made of the precursor powders during sintering like reduction of particle size, reduction of the oxygen impurity, increase of the defect concentrations, addition of the second phases and dopants, applying pressure and temperature simultaneously, etc.

Carbide of zirconium (ZrC) is a new potential material for ultra high temperature applications like hypersonic re-entry vehicles, space shuttles and also other conventional application like thermal, nuclear power plant, high temperature crucible, electrodes etc.

For making real life components, proper synthesis of phase pure ZrC composition from the precursors and sintering either in bulk form or coating form is essential. From the above review regarding synthesis and sintering of ZrC, following conclusions may be drawn:

Phase pure ZrC was prepared by mixing of elemental Zr and carbon through SHS process, but due to high cost and difficult to handle highly reactive Zr metal, carbothermal reduction is an effective alternative to obtain phase pure ZrC and other composites. The reactivity of carbothermal reduction through gas phase diffusion transport leads to pronounced change in temperature, product shape and reactants-to products conversion efficiency. Alternative novel solution based processing routes like sol gel and polymer precursor synthesis produce nano-size powders at relatively lower temperature. The main drawbacks like low fluidability and very low ceramic yield, and they are costly, those restrict its application in fabrication of real life UHTC components in bulk quantity. However, chemical vapour deposition is a convenient process used to prepare high purity, oxygen free thin hard and oxygen resistive coatings on different substrats like graphite, carbon tube, alloys, etc. Compared with conventional chemical technique, infiltration method is a novel method for fabrication of complex shaped ZrC based composites and large scale production at relatively lower temperature. More advanced research is going on for further reduction of particle size, increasing purity level of the powder, decreasing temperature and cost of the overall synthesis process.

Pressureless sintering is a simple and economic sintering process for ZrC especially at high temperature, depending on compositions. In general the *pressureless sintering* process is performed by green compaction followed by sintering at temperature under ambient or controlled atmosphere. For making monolithic ZrC, hot pressing or spark plasma sintering is generally used for better densification. But complex shaped components can not be fabricated by this technique. Sometimes, metallic additives like Ni, Mo, W etc or other liquid forming agents like TaSi₂, MoSi₂ etc. have been used for enhancing the densification at relatively lower temperature. But the formation of liquid phase compounds reduces the mechanical and tribological properties at high temperature above 1200 °C. To overcome this limitation, researchers used ceramic additives like SiC, B₄C, Si₃N₄, Al₂O₃, VC, TaC, NbC, etc. for improving the mechanical and tribological properties especially at high temperature.

Finally, for making actual shape of complex geometry, machining like wire electro discharge machining or die-sinking electro discharge machining can be applied to sintered and electrically conductive ZrC bulk samples.

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