

CVD Growth of ZrC Layers at Different Temperatures

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Abstract Zirconium carbide (ZrC) layers were grown on a graphite substrate by chemical vapour deposition (CVD) at 1250°C, 1300°C and 1350°C. Zirconium tetrachloride (ZrCl₄), methane (CH₄), hydrogen (H₂) and argon (Ar) were used as precursors. The deposited ZrC layers were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD showed ZrC characteristic peaks with free carbon. Free carbon incorporated in the ZrC layer increased with deposition temperature. The average of grain size also increased with deposition temperature. The latter findings were confirmed by SEM results.

Keywords: chemical vapour deposition (CVD), ZrC, XRD, SEM

Cite This Article: BAB Alawad, S Biira, H Bissett, JT Nel, TT Hlatshwayo, PL Crouse, and JB Malherbe, "CVD Growth of ZrC Layers at Different Temperatures." *Physics and Materials Chemistry*, vol. 4, no. 1 (2016): 6-9. doi: 10.12691/pmc-4-1-2.

1. Introduction

Zirconium carbide (ZrC) has an appearance of grey color with cubic, type structure (fcc), ZrC is a very important refractory material in industry. It has been used as a coating on atomic fuel particles for nuclear fusion power plants, in cutting tools and electronic devices [1,2]. ZrC coatings have been grown by different method such as laser cladding [3], pulsed laser ablation deposition [4], magneto sputter deposition [5], electron beam bombardment [6], and chemical vapour deposition (CVD) [4,6]. Among these methods CVD is considered to be the best method because it can grow uniform coatings which are less porous. It, therefore, is the most investigated deposition method for the preparation of ZrC coatings.

Several different precursors have been used to grow ZrC layers using CVD. These include chloride (ZrCl₄), bromide (ZrBr₄), and iodide (ZrI₄) [7,9]. The different parameters such as temperature, deposition pressure, carbon source, and flow rate of gas precursors have also been examined [10]. A previous study [11] reported on ZrC layers grown at different temperatures by a low pressure chemical vapour deposition (LPCVD) system using ZrCl₄, CH₄, and H₂ as precursors. Thermodynamic investigations of the ZrC layer deposition process have also been carried out [12].

In a closely related experiment to ours, Lui et al. [13] synthesised ZrC layers using CH₄, ZrCl₄, Ar and H₂ as precursors. They used a horizon hot-wall deposition apparatus contrast to our vertical reaction chamber. The deposition morphologies and deposition rates were studied at different temperature to understand the deposition mechanisms [13].

In CVD processing the growth temperature is an important parameter that influences the properties of the

grown layers. Therefore, in this study, ZrC layers were grown using an in-house built CVD reactor at 1250°C, 1300°C and 1350°C. Methane (CH₄) was used as a carbon source and zirconium tetrachloride (ZrCl₄) as a zirconium source. Hydrogen (H₂) was added to participate in the conversion reaction while argon (Ar) was used as flowing/carrier agent for the zirconium tetrachloride (ZrCl₄). The deposition of ZrC layer and deposition rate were investigated at 1250°C, 1300°C and 1350°C to understand the deposition mechanisms.

2. Experimental Procedure

The deposition of ZrC was performed using the CVD system shown in Figure 1. In this CVD system, radio frequency (RF) induction heating was used to heat a graphite tube of length 300 mm, outer diameter of 35 mm, and inner diameter 25 mm. The vertical tube was steel with an inner diameter of 2.5 cm outer diameter of 3.3 cm and length of 11 cm. The ZrC layers were deposited at 1250°C, 1300°C and 1350°C using ZrCl₄, CH₄, H₂ and Ar as precursors. The purities of the precursors and deposition parameters are listed in Table 1. The ZrCl₄ was put in the steel tube to vaporize. When the temperature of the furnace (including the steel tube) reached 300°C for 5 minutes the steel tube started to vaporize ZrCl₄.

Argon gas carried the ZrCl₄ vapour to a graphite substrate in the coating chamber. CH₄ mixed with H₂ was fed into the coating chamber. The duration of the growth reaction was about 2 hours. The phases of the layers were characterized by XRD diffraction, which was carried out by using radiation CuK α wavelength 1.5406 nm in a Bruker AXS D8 Advance diffractometer. The morphologies of the ZrC layers on graphite substrates were observed by SEM Zeiss Ultra Plus.

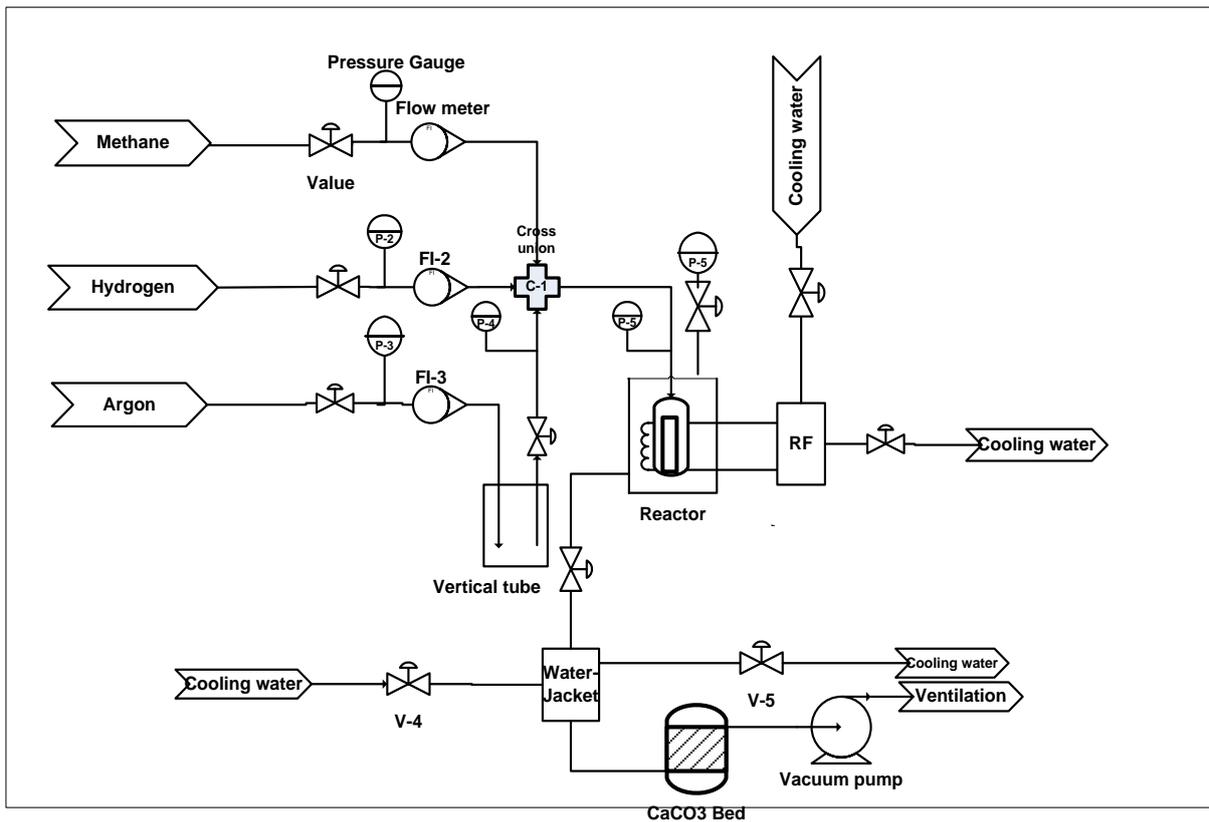


Figure 1. A schematic diagram of the induction heating radio frequency (RF) Chemical Vapour Deposition (CVD) system to grow ZrC layers on graphite substrates

Table 1. The purities of the precursors and deposition parameters

Deposition precursors	ZrCl ₄	CH ₄	H ₂	Ar
Purity	99.95%	99.95%	99.95%	99.95%
Flow rates	1g/h	38.5 sccm	853 sccm	562 sccm
Deposition temperature	1250°C, 1300°C and 1350°C			
Gauge pressure	-5 kPa			
Deposition time	2 hours			

3. Results and Discussion

$$K = M / tA\rho \quad (1)$$

3.1. Deposition Rate of ZrC Layer

The deposition rate of ZrC layer (K) was calculated using the mass increase of the substrate. The layer thickness was estimated by:

where M is mass of the ZrC layer, A is the surface area, ρ is the density of ZrC (6.73 Kg m⁻³) and t is deposition time. The experimental parameters and results are summarised in Table 2.

Table 2. The experimental parameters and results of the CVD deposition process

Temperature (°C)	CH ₄ flow rate (sccm)	H ₂ flow rate (sccm)	Ar flow rate (sccm)	ZrCl ₄ flow rate (gh ⁻¹)	Molar ratio CH ₄ /ZrCl ₄	Deposition rate (µm/h)	Grain size (nm)
1250	38.5	853	562	1	7.6	4.3	16.7
1300	38.5	853	562	1	8.02	5.8	21.6
1350	38.5	853	562	1	8.3	7.6	25.4

Table 2 shows that with increasing temperature and CH₄/ZrCl₄ molar ratio the deposition rate and average grain size increased.

3.2. XRD Discussions

Figure 2 shows XRD patterns of ZrC layers prepared by chemical vapour deposition (CVD) at 1250°C, 1300°C and 1350°C. The XRD peaks were matched with standard data for ZrC (JCPD card No. 35-0784). The peaks located at 2 θ values (degrees) of 32.93, 38.20, 55.13, 65.73, 69.05, 81.76, 90.99, 94.06, 106.56, 116.47, 116.47, 135.51 were found to correspond to the (111), (200), (220), (311),

(222), (400), (331), (420), (422) and (511) planes respectively. Carbon peaks were also detected and are indicated by C in Figure 2. The carbon peaks were more visible at 1350°C which was the highest deposition temperature of this study. ZrC peaks became narrower as temperature increased from 1250°C to 1350°C. The various decomposition rates for ZrCl₄ and CH₄ may be the reason for the composition difference of Zr and C at the different temperatures used in this study. With increasing temperature, CH₄ becomes easier to decompose at higher temperatures, which will subsequently increase the amount of free carbon in the ZrC layer.

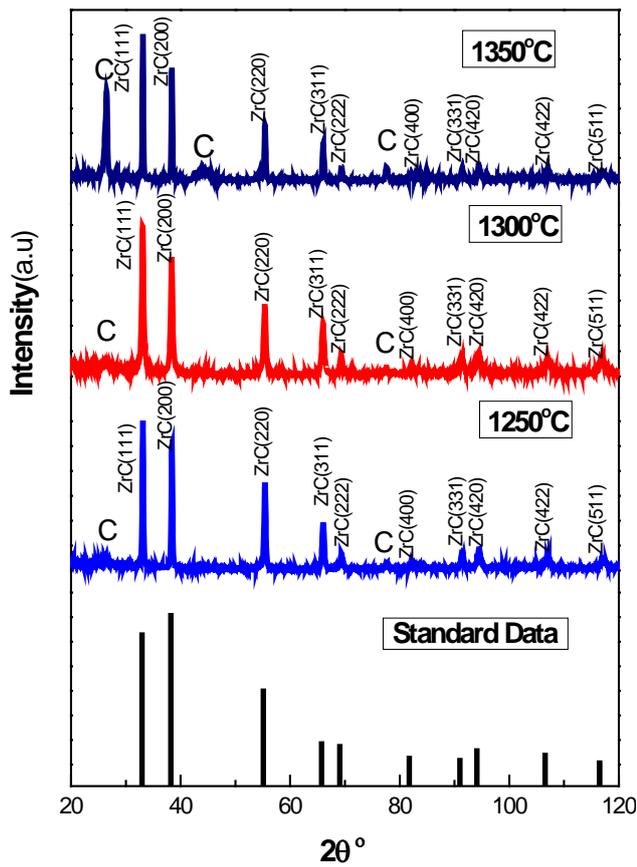


Figure 2. XRD patterns of ZrC layers deposited at 1250°C, 1300 °C and 1350°C

The average grain size D of ZrC deposited at the different temperatures were determined from Scherrer's equation [15]:

$$D = K\lambda / B \cos \theta \quad (2)$$

where B is the full width at half maximum (FWHM) of the peak, θ is the Bragg angle, K is a constant (a value of 0.94 was used), and $\lambda = 1.54$ nm is the wavelength of the excitation X-rays. The calculated average of grain size increased from 16.7 nm to 21.6 nm and to 25.4 nm when the temperature increased from 1250°C to 1300°C and to 1350°C respectively. This was due to the increase in the mobility of the atoms and the increase of the diffusion length of reactive atoms [11].

3.3. SEM Results

Figure 3 shows the SEM micrographs of the ZrC layers deposited at different temperatures. ZrC deposited at 1250°C had a fairly smooth surface with small grains in Figure 3(a). ZrC deposited at 1300°C showed larger grains that are prominently distributed on the surface in Figure 3(b). Also visible in the SEM are some clusters of ZrC crystallites on top of the surface. The clusters consist of multiple twinned ZrC crystals due to heterogeneous nucleation in the vapour phase. Almost similar results were observed for the 1350 °C grown layer even though the grains were slightly less pronounced than for the 1300 °C grown layers. This might due to the more free carbon in the layers as can be seen the XRD results, i.e. in Figure 2.

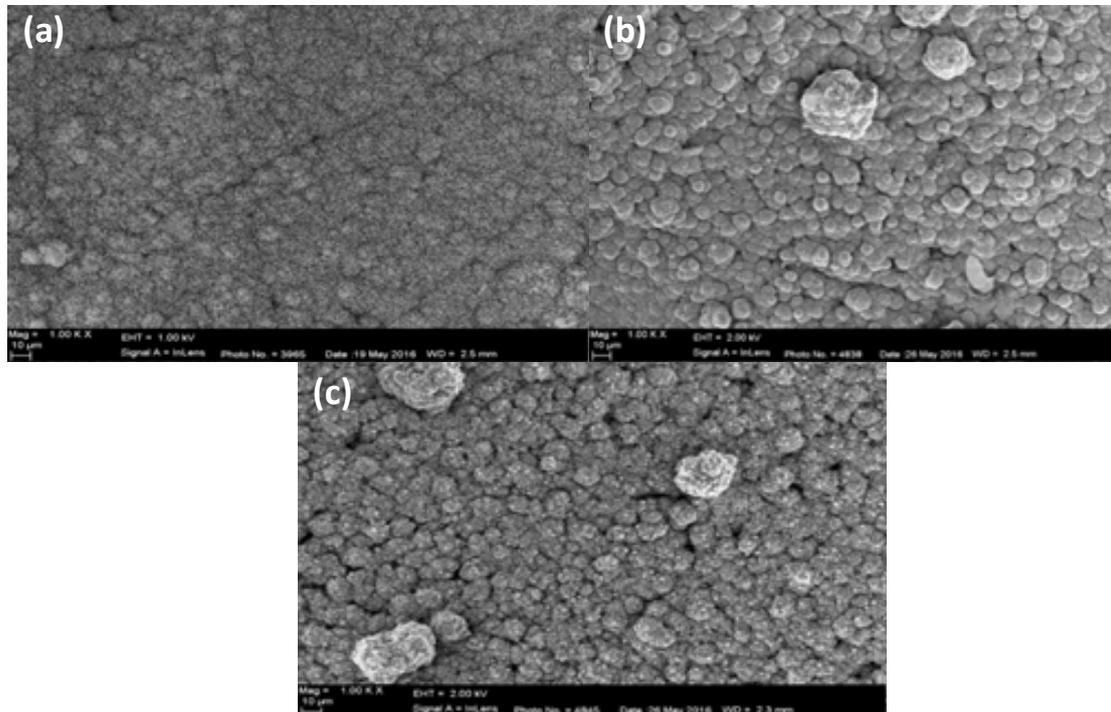


Figure 3. SEM images of ZrC deposited at different temperatures

4. Conclusions

In this paper, zirconium carbide (ZrC) layers were prepared by chemical vapour deposition (CVD) using $ZrCl_4$, CH_4 , H_2 and argon Ar as precursors at different temperatures. The growth rate was determined using the

increase on mass of the samples and was found to increase with increasing temperature. Layer composition was determined by XRD. The typical reflections for ZrC were observed. The grains size for ZrC layers were calculated by the Scherrer method while the morphologies of ZrC layers were observed by scanning electron microscopy (SEM). In general, the grains size and surface topography

increases with increasing temperature. The free carbon content in the ZrC films as measured by XRD, increased with increasing temperature.

Acknowledgment

This work is financially supported by Nuclear Energy Corporation South Africa (Necsa) and then I would also like to acknowledge support by the University of Pretoria and the Sudan University of Science and Technology, Khartoum, Sudan.

References

- [1] F. Charollais, S. Fonquernie, C. Perrais, M. Perez, O. Dugne, F. Cellier, G. Harbonnier, and M.-P. Vitali, "CEA and AREVA R&D on HTR fuel fabrication and presentation of the CAPRI experimental manufacturing line," *Nucl. Eng. Des.*, vol. 236, no. 5, pp. 534-542, 2006.
- [2] H. O. Pierson, *Handbook of chemical vapor deposition: principles, technology and applications*. William Andrew, 1999.
- [3] T. Xie, W. A. Mackie, and P. R. Davis, "Field emission from ZrC films on Si and Mo single emitters and emitter arrays," *J. Vac. Sci. Technol. B*, vol. 14, no. 3, pp. 2090-2092, 1996.
- [4] Q. Zhang, J. He, W. Liu, and M. Zhong, "Microstructure characteristics of ZrC-reinforced composite coating produced by laser cladding," *Surf. Coatings Technol.*, vol. 162, no. 2, pp. 140-146, 2003.
- [5] L. D'Alessio, A. Santagata, R. Teghil, M. Zaccagnino, I. Zaccardo, V. Marotta, D. Ferro, and G. De Maria, "Zirconium carbide thin films deposited by pulsed laser ablation," *Appl. Surf. Sci.*, vol. 168, no. 1, pp. 284-287, 2000.
- [6] C.-S. Chen, C.-P. Liu, and C.-Y. Tsao, "Influence of growth temperature on microstructure and mechanical properties of nanocrystalline zirconium carbide films," *Thin Solid Films*, vol. 479, no. 1, pp. 130-136, 2005.
- [7] T. Ogawa, K. Ikawa, and K. Iwamoto, "Chemical vapor deposition of ZrC within a spouted bed by bromide process," *J. Nucl. Mater.*, vol. 97, no. 1, pp. 104-112, 1981.
- [8] K. Ikawa, "Vapor deposition of zirconium carbide-carbon composites by the chloride process," *J. Less Common Met.*, vol. 29, no. 3, pp. 233-239, 1972.
- [9] J. A. Glass, N. Palmisiano, and R. E. Welsh, "The chemical vapor deposition of zirconium carbide onto ceramic substrates," in *MRS Proceedings*, 1998, vol. 555, p. 185.
- [10] T. Ogawa, K. Ikawa, and K. Iwamoto, "Effect of gas composition on the deposition of ZrC-C mixtures: The bromide process," *J. Mater. Sci.*, vol. 14, no. 1, pp. 125-132, 1979.
- [11] J. H. Park, C. H. Jung, D. J. Kim, J. Y. Park, "Temperature dependency of the LPCVD growth of ZrC with the ZrCl₄-CH₄-H₂ system," *Surf. Coatings Technol.*, vol. 203, no. 3, pp. 324-328, 2008.
- [12] A. K. Pattanaik and V. K. Sarin, "Basic principles of CVD thermodynamics and kinetics," *Chem. Vap. Depos. Surf. Eng. Ser.*, vol. 2 (2000): 23.
- [13] Q. Liu, L. Zhang, L. Cheng, and Y. Wang, "Morphologies and growth mechanisms of zirconium carbide films by chemical vapor deposition," *J. Coatings Technol. Res.*, vol. 6, no. 2, pp. 269-273, 2009.
- [14] S. Biira, B. A. B Alawad, H. Bissett, J. T. Nel, T. T. Hlatshwayo, P. L. Crouse, and J. B. Malherbe, "Synthesis of ZrC coatings in an RF induction-heating CVD system," *Thin Solid Films*, Submitted, 2016.
- [15] R. Delhez, Th. H. De Keijser, and E. J. Mittemeijer, "Determination of crystallite size and lattice distortions through X-ray diffraction line profile analysis," *Fresenius' Zeitschrift für Anal. Chemie*, vol. 312, no. 1, pp. 1-16, 1982.