Thin Solid Films 624 (2017) 61–69

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Optimisation of the synthesis of ZrC coatings in a radio frequency induction-heating chemical vapour deposition system using response surface methodology

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ARTICLE INFO

Article history:
Received 19 May 2016
Received in revised form 10 January 2017
Accepted 11 January 2017
Available online 12 January 2017

Keywords:
Zirconium carbide
Chemical vapour deposition
Substrate temperature
Methane
Zirconium chloride
Response surface model
Growth rate
Crystallite size
Energy-dispersive X-ray spectroscopy

ABSTRACT

A chemical vapour deposition process using radio frequency induction heating operating at atmospheric pressure was developed for the deposition of ZrC coatings. The precursors utilised in this process were zirconium tetrachloride and methane as zirconium and carbon sources respectively, in an excess of hydrogen. Additionally, a stream of argon was used to, first, remove oxygen from the reactor and then to sweep the vapourised $ZrCl_4$ at 300 °C to the reaction chamber. The ZrC coatings were deposited on graphite substrates at substrate temperatures in the range of 1200 °C–1600 °C. The molar ratio of $CH_4/ZrCl_4$ was varied from 6.04 to 24.44. Before the start of the deposition process, thermodynamic feasibility analysis for the growth of ZrC at atmospheric pressure was also carried out. Response surface methodology was applied to optimise the process parameters for the deposition of ZrC coatings. A central composite design was used to investigate the effects of temperature and molar ratio of $CH_4/ZrCl_4$ on the growth rate, atomic ratio of C/Zr and crystallite size of ZrC coatings. Quadratic statistical models for growth rate and crystallite size were established. The atomic ratio of C/Zr followed a linear trend. It was found that an increase in substrate temperature and $CH_4/ZrCl_4$ ratio resulted in increased growth rate of ZrC coatings. The carbon content (and concomitantly the atomic ratio of C/Zr) in the deposited coatings increased with temperature and molar ratio of $CH_4/ZrCl_4$. The substrate temperature of 1353.3 °C and the $CH_4/ZrCl_4$ molar ratio of 10.41 were determined as the optimal condition for growing near-stoichiometry ZrC coatings. The values were 1.03, 6.05 μm/h and 29.8 nm for C/Zr atomic percentage ratio, growth rate and average crystallite size respectively.

1. Introduction

Generation IV high temperature nuclear reactors use TRISO (tristructural isotropic) particles for containment of radioactive fission products [1]. TRISO particles consist of uranium oxide coated uniformly with low density pyrocarbon, high density inner pyrocarbon, silicon carbide (SiC), and dense outer pyrocarbon [2]. In these particles SiC is the main barrier for containing solid fission products. These particles retain most fission products with the exception of silver at temperatures below 1000 °C. In a recent review paper by Malherbe on SiC [3], the problems of the diffusion of silver and other fission products in SiC was extensively discussed. In the same review, it was suggested that it would be advantageous to add a thin ZrC layer (in addition to the normal SiC layer) to the TRISO layer system because it is a better barrier than SiC against Ag diffusion and is more resistant against palladium attack [4,5].

ZrC has a high melting temperature of 3540 °C, and relatively low vapour pressure compared to SiC, which begins to decompose at 1500 °C [6]. ZrC also has a low neutron capture cross section, good thermal shock resistance, relatively low density, excellent thermal stability, and high hardness [7,8]. It is important to note that the properties of ZrC coatings depend on a number of factors such as chemical composition, crystallite size and morphology, orientations of crystal planes, structural defects, porosity, and the presence of impurities. These factors are a function of the methods and conditions used in growing ZrC coatings. Chemical vapour deposition (CVD) produces coatings with very low levels of impurities and low porosity [9], which is why it is the preferred method.

Compared to SiC, little research has been published on the use of ZrC in nuclear reactors. The main reason is probably that SiC has proven nuclear applications, and other desirable physical properties (e.g. a wide

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http://dx.doi.org/10.1016/j.tsf.2017.01.018
0040-6090/

bandgap semiconductor, it's the second hardest natural material, etc.). Another reason for this might be that it is difficult to grow good quality ZrC.

In this study, the aim is to introduce a statistical optimisation method to grow ZrC coatings in a CVD system using a response surface methodology. This method allows one to determine the deposition parameters for obtaining specific coating properties, e.g. ZrC coatings with a specific composition. This has not yet been reported for ZrC film growth. The paper also details the development of a deposition process for the preparation and optimisation of ZrC coatings from $ZrCl_4$-Ar-CH_4-H_2 precursors using induction thermal CVD at atmospheric pressure. The objectives were: (1) to fabricate and develop the CVD system; and (2) to investigate the microstructure and composition of ZrC coatings deposited as a function of the input variables. In this study ZrC coatings were produced by CVD at temperatures ranging from 1200 °C to 1600 °C and CH_4/$ZrCl_4$ molar ratios from 6.04 to 24.44. After choosing temperature and the CH_4/$ZrCl_4$ ratio as the most important variables influencing the properties of ZrC, in order to achieve optimum conditions for growing ZrC coatings, a statistical experimental design methodology (central composite design) was applied to explore the effects of these variables [10]. Other deposition conditions such as total reactor pressure, deposition time, reactor geometry, hydrogen flow and carrier gas and its flow have been maintained constant throughout this experimental process.

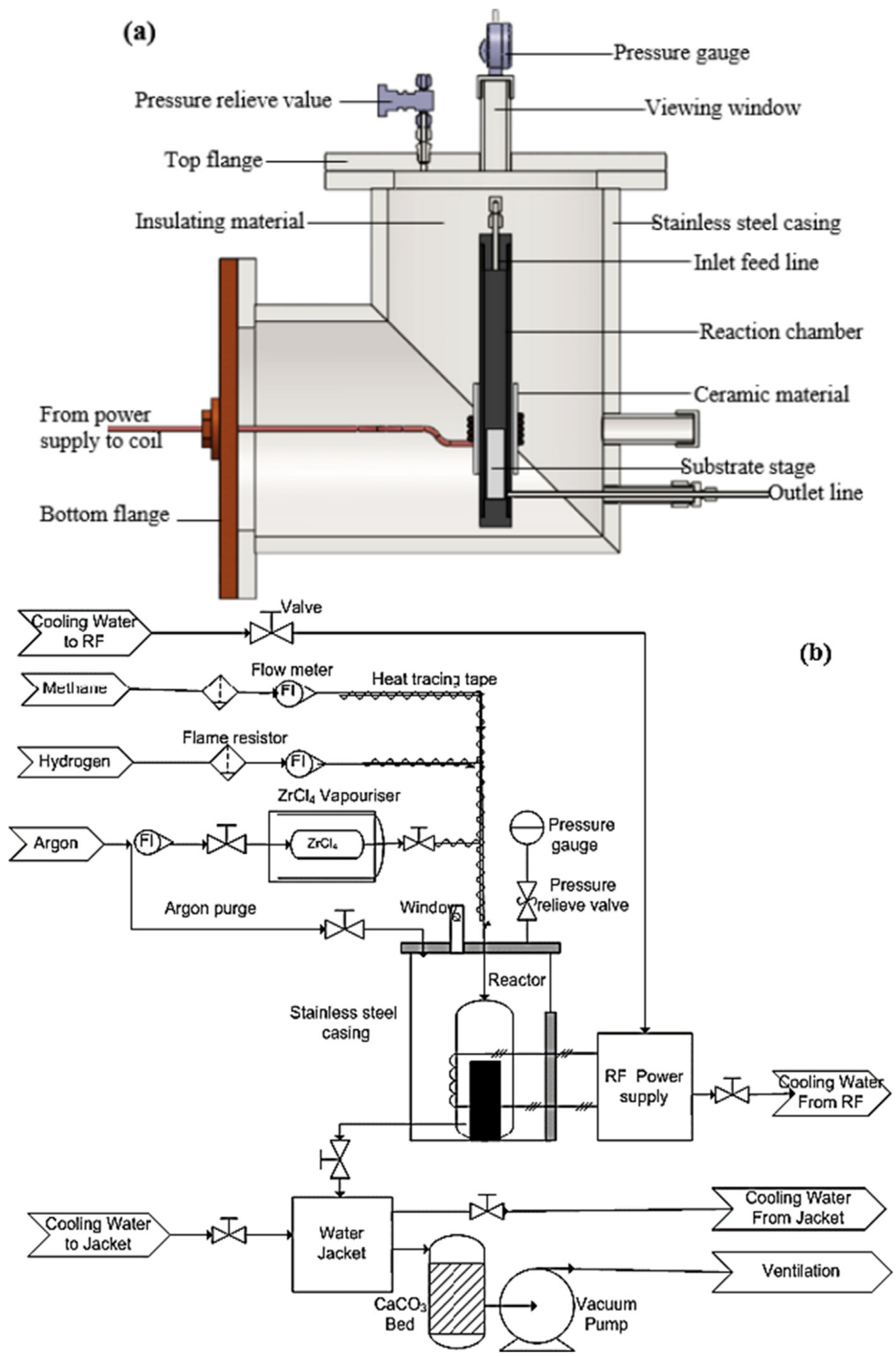

Fig. 1. (a) Schematic diagram of the CVD reactor system. (b) Process and instrumentation diagram for the CVD reactor set-up.