Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

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

Deposition, characterization and high-temperature steam oxidation behavior of single-phase Ti_2AlC-coated Zircaloy-4

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ARTICLE INFO

Keywords:
A. Sputtered films
A. Zirconium
B. SEM
C. High temperature corrosion
C. Oxidation

ABSTRACT

Oxidation of single-phase and dense Ti_2AlC coatings with or without a 500 nm TiC diffusion barrier deposited on Zircaloy-4 by annealing of nanoscale multilayer stacks between 800 °C and 1200 °C in high-temperature steam was investigated. Coatings without TiC barrier formed a duplex scale: outer θ-Al_2O_3 rich layer mixed with TiO_2 and inner porous TiO_2 layer; correspondingly, a triple-layered scale (θ-Al_2O_3 + TiO_2/θ-Al_2O_3/TiO_2) grew on coatings with barrier at 800 °C. The TiC barrier suppresses the rapid diffusion of Al into the substrate, contributing to improved performance and longer life of Ti_2AlC/TiC coatings. However, both coatings demonstrated low protection effect from 1000 °C in steam.

1. Introduction

Nuclear power provides around 13% of the world's electricity with over 400 nuclear reactors in operation worldwide. The majority of these reactors are water-cooled reactors [1]. Zirconium-based alloys, like Zircaloy-4 and M5®, are currently utilized as fuel cladding and structural components in these commercial reactors due to their low thermal neutron absorption cross section, good mechanical properties and reasonable corrosion resistance during operation conditions [2]. In general, the corrosion of the cladding by coolant water results in initial formation of a dense, adherent oxide layer following a cubic rate growth law. Once the oxide layer exceeds a certain critical thickness, fracture of the oxide layer takes place, leading to a large number of cracks in the oxide. The growth kinetics transforms to a linear law with accelerated corrosion rate [3]. Moreover, hydrogen generated by the corrosion reaction between zirconium and water can be absorbed by the cladding and eventually precipitate as hydrides, leading to the hydride embrittlement of the cladding. Hydride formation can strongly degrade the cladding performance during design-basis (DB) and beyond design-basis (BDB) accident scenarios [3]. One additional undesirable feature of zirconium-based cladding is their extremely fast oxidation kinetics with high-temperature steam during loss of cooling accidents (LOCA) [4]. A considerable amount of heat and hydrogen gas is produced by the reaction of zirconium and steam. The heat generated by the steam oxidation reaction becomes comparable to or even exceeding the decay heat. In a serious situation, like station blackout (SBO), the core suffers severe degradation and hydrogen explosion can occur, followed by subsequent release of highly-radioactive fission products to the environment like during the nuclear accidents at the Fukushima Daiichi Nuclear Power Plant in 2011 [5].

The concept of accident tolerant fuels (ATF) moved into the focus of international research after Fukushima, aiming at providing substantially improved safety margins and increasing coping time during severe accidents while maintaining the fuel performance under normal operating conditions [6]. Different strategies are being investigated. One approach is to develop oxidation resistant bulk materials, like SiC-based composite, FeCrAl alloys, and triplex molybdenum cladding replacing current zirconium-based alloy claddings [6–8]. An alternative strategy is the protection of state-of-the-art zirconium-based alloy fuel claddings with an oxidation resistant coating. This solution promises the elimination of the hydrogen pickup during normal operation, as well as significant improvement of the reaction kinetics with steam during off-normal conditions. Different types of coating materials, mainly TiO_2-, Al_2O_3- or Cr_2O_3- forming, are being investigated [9–13].

$M_{n+1}AX_n$ (or MAX) phases, where M is an early transition metal, A is an A-group, mostly groups IIIA and IVA, element and X is either C and/or N, n = 1–3, represent hexagonal carbides and nitrides consisting of a nanolaminated structure [14]. These compounds combine many attractive properties of both ceramics and metals, such as lightweight, machinability, damage tolerance and thermal shock resistance, as well as excellent thermal conductivity. Al-containing MAX phases, like Ti_2AlC, Ti_3AlC_2, Cr_2AlC, are promising coating materials because of

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https://doi.org/10.1016/j.corsci.2018.02.035
Received 18 May 2017; Received in revised form 3 February 2018; Accepted 16 February 2018

their excellent high-temperature oxidation resistance both in air and steam, self-healing in an oxygen-containing service environment as well as with outstanding mechanical properties and irradiation stability [15–18]. In previous studies relatively thick (dozens of micrometers) Ti_2AlC coatings were deposited on zirconium-based alloys by cold spray [19] or high velocity oxy-fuel (HVOF) [20]. Therefore, the structure of the coatings was loose consisting of a large amount of TiC and/or TiAl intermetallic secondary phases. These phases have been proved to reduce the oxidation resistance of the Ti_2AlC materials. Yeom et al. recently deposited Ti_2AlC coatings on Zircaloy-4 substrate by dc magnetron sputtering with following laser surface annealing at 900 °C in order to maintain the substrate microstructure. However, formation of microcracks was observed within the coatings after surface annealing [21].

In our previous study, an elemental nano-multilayer stack deposited by non-reactive magnetron sputtering followed by ex-situ annealing was adopted to prepare Ti_2AlC coatings. The microstructural evolution of the coatings during ex-situ annealing from 600 °C to 900 °C was systematically investigated and the results demonstrated that phase-pure, i.e. single-phase polycrystalline Ti_2AlC coatings on SiO_2/Si were obtained after 800 °C annealing in argon for 10 min [22]. This work attempted to synthesize the phase-pure polycrystalline Ti_2AlC MAX phase coatings on polished Zircaloy-4 substrates by the same approach using non-reactive magnetron sputtering of elemental multilayer thin films with a multiple stacking sequence of titanium, – carbon, and – aluminum layers from three element targets, and subsequent thermal annealing in argon at 800 °C. The overall coating thickness was around 5.5 µm with or without a 500 nm thickness TiC diffusion barrier. Single-phase and dense Ti_2AlC coatings were obtained after annealing at 800 °C below the phase transformation temperature of Zircaloy-4 substrates. The microstructure, adhesion and mechanical properties of the coatings were evaluated using X-ray diffraction, scanning electron microscopy, Raman spectroscopy, hardness test and scratch test methods. The performance of the coatings in high-temperature steam from 800 °C to 1200 °C was examined and compared to bare Zircaloy-4 samples and bulk Ti_2AlC ceramic.

2. Material and methods

Square Zircaloy-4 (Zry-4) alloy specimens ($\sim 10 \times 10 \times 0.60\ mm^3$) cut from a large plate were used as substrates in the present study. The chemical composition (wt.%) of the Zircaloy-4 was as follows: Sn ~1.4, Cr ~0.10, Fe ~0.22, O ~1000 ppm, Zr bal. The specimens were firstly ground with SiC paper, followed by polishing using diamond paste, and finally rinsed with active oxide polishing suspensions and water. The finished surface roughness (Ra) was around 50 nm. An elemental nanoscale multilayer approach was used to prepare the Ti_2AlC MAX phase coatings. Fig. 1 shows the schematic of the design of the multilayer system. The multilayer stacks were deposited by non-reactive magnetron sputtering using a laboratory Leybold Z 550 coater from three elemental targets. The periodical stack (with a thickness of ~14 nm) has been repeated until a desired total film thickness was obtained. The overall coating thickness was around 5.5 µm (Fig. 1a). For one batch of coatings, a 500 nm thick Ti-C multilayer was deposited as diffusion barrier (Fig. 1b). The substrates were ultrasonically cleaned in acetone bath for 10 min before being introduced into the deposition chamber. The base pressure was around 1×10^{-4} Pa and the working pressure of the Ar gas during deposition was kept at 0.5 Pa, respectively. The substrates were plasma-etched with R.F. power of 500 W for 15 min prior to deposition. All three targets were at a target power of 200 W, R.F. for titanium and aluminum targets and D.C. for carbon target. During deposition, the PVD facility ran in a stop-and-go mode, and the overall deposition rate was around 1 µm per hour. Only the two main sides of the substrates were coated. For detailed information on the synthesis of the coatings, please refer to reference [22].

After deposition, the coatings were ex-situ annealed in pure Ar (99.9999%) at 800 °C for 10 min using a commercial thermal balance (NETZSCH STA-449) to yield the formation of Ti_2AlC MAX phase. The heating and the cooling rates were fixed at 10 K/min. The composition of the as-deposited coatings was measured by electron probe microanalysis (EPMA) with a Cameca microbeam system. An average value based on four measurements located in different regions was taken. The crystalline structures of the coatings, including the as-deposited and annealed, was analyzed by X-ray diffraction (XRD, Seifert PAD II diffractometer), and Raman spectroscopy (Renishaw Raman 1000). The XRD signals were collected in Bragg–Brentano geometry with CuKα radiation ($\lambda = 1.54$ Å) at a voltage of 40 kV and a current of 30 mA. The Raman spectra were collected and recorded between 160 and 2000 cm^{-1} using an Argon-ion laser with wavelength 514.5 nm and power 2–3 mW. The indentation hardness and reduced Young's modulus of the coatings were measured with a Berkovich nano-indenter (UMIS 2000). During the indentation test, the indentation depth was adjusted to be significantly higher than the surface roughness but less than 1/10 of the total film thickness to avoid substrate effects. The values reported herein represent the average based on at least ten indentations per sample. The coating-substrate adherence was evaluated by scratch tests (CSM Revetest) applying an increasing load of 20 N/cm up to 80 N and further determination of the critical load from the micrographs of the scratches. The scratch tests were repeated for three times to obtain an average and accurate results.

The performance of the coatings in high-temperature steam from 800 °C to 1200 °C was examined also using the NETZSCH STA-449 thermal balance with a steam furnace. The bare Zircaloy-4 samples and a commercial Maxthal 211® bulk ceramic (nominally Ti_2AlC, Kanthal/Sweden) were tested under the same conditions for comparison. After oxidation, the surface oxide scale was characterized by XRD using the same setup as before. The surface and cross-section microstructures were analyzed by an optical microscope (OM, Reichert-Jung MeF), as well as by a field-emission scanning electron microscope (SEM, Philips XL30S) equipped with an energy dispersive X-ray spectroscopy (EDS) detector for element analysis. For cross-sectional examination, the

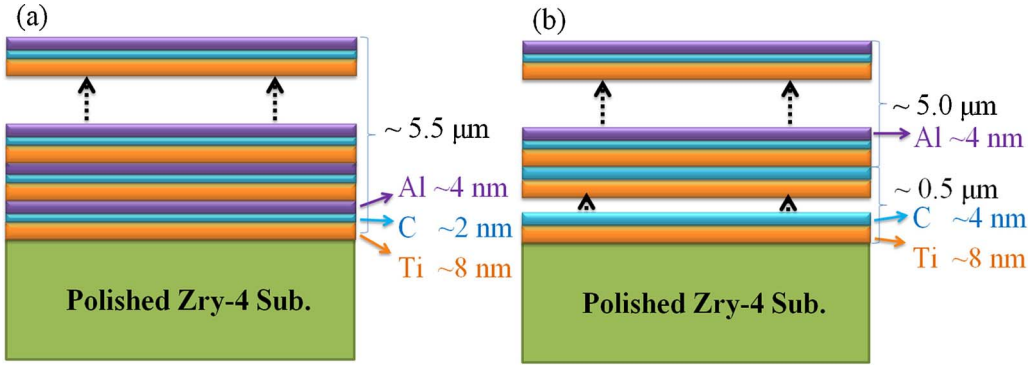

Fig. 1. Schematic of the elemental nanoscale multilayer stacks on polished Zry-4 substrates. (a) without Ti-C barrier, (b) with around 500 nm thick Ti-C barrier.