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Magnetron sputter deposition of zirconium-silicide coating for mitigating high temperature oxidation of zirconium-alloy

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ABSTRACT

The air oxidation behavior of zirconium-silicide coatings for three stoichiometries, namely, Zr_2Si, ZrSi, and $ZrSi_2$, at 700 °C has been investigated. These three coatings were deposited on a zirconium-alloy substrate using a magnetron sputter process at a low temperature. Argon gas pressure was observed to have a profound effect on the coating microstructure, with lower pressures favoring a denser and more protective microstructure. Coatings of $ZrSi_2$ stoichiometry clearly showed superior oxidation resistance presumably due to the formation of a thin protective oxide layer, consisting of nanocrystalline SiO_2 and $ZrSiO_4$ in amorphous Zr-Si-O matrix. The thermal stability of the coatings was evaluated by annealing in an argon environment, and this also assisted in eliciting the effects of oxidation-induced inward Si migration. Thicker coatings of $ZrSi_2$ were prepared and evaluated for oxidation resistance at 700 °C for longer exposure times, as well as at 1000 °C and 1200 °C. Once again the thin oxide layer provided for significant oxidation resistance. Pre-oxidizing the samples at 700 °C prior to 1000 °C and 1200 °C oxidation tests substantially reduced the extent of oxidation. Insights into the fundamental mechanisms of the oxidation behavior of zirconium-silicide coatings were obtained using a combination of scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy techniques. One potential application of these coatings is to enhance the oxidation resistance of zirconium-alloy fuel cladding in light water reactors under normal and accident conditions.

1. Introduction

Coatings of structural material for elevated temperature applications are becoming increasingly important in a broad spectrum of industries including, aerospace, power generation, and chemical plants. In particular, long term exposure of base materials in high temperature air environment undermines inherent mechanical properties by chemical reaction with ambient oxygen and moisture. For example, the exothermic reaction of zirconium-alloy and high temperature air or steam in high temperature leads to loss of intrinsic mechanical properties due to thick oxide layer formation and hydrogen embrittlement [1–3]. Transition metal silicides, particularly molybdenum-silicide ($MoSi_2$) have been extensively used as coatings for graphite, Molybdenum, and Niobium structural material in the high temperature applications due to its excellent oxidation resistance and mechanical properties [4–6]. However, there is very limited literature on zirconium-silicide in regards to oxidation or in its use as a coating material. Zirconium silicides (Zr_xSi_y) have high melting points (e.g., ZrSi and Zr_3Si_2 melts at 2203 °C and 2215 °C, respectively [7]). In high temperature air, formation of a passive oxide layer, outstanding oxidation resistance SiO_2 and $ZrSiO_4$, suggest that zirconium-silicide could be good candidate oxidation resistant coating material for high temperature applications [8,9]. In particular, the application of zirconium-silicide coatings on zirconium alloys appears logical given the inherent compatibility between the coating and substrate materials, and no previous studies have been reported on the oxidation behavior of this particular coating-substrate system.

In this study, magnetron sputter deposition of zirconium-silicide on Zircaloy-4 substrate has been explored. To maximize oxidation resistance, deposition parameters and coating compositions have been investigated with characterization of oxidation behavior at 700 °C in air and of thermal stability at 700 °C in argon environment. A temperature of 700 °C was selected to avoid excessive substrate oxidation and to evaluate a formation of non-protective oxide scale like $MoSi_2$ [4,10]. Finally, the optimized zirconium-silicide coating was prepared and oxidized at 1000 °C and 1200 °C in ambient air to evaluate oxidation resistance, which demonstrates potential feasibility of the zirconium-

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silicide coating for zirconium-alloy cladding in light water reactors under potential accident scenarios.

2. Experimental procedure

Test flat coupons of Zircaloy-4 (referred to henceforth as Zirc-4, nominal composition: 0.07 wt% Cr, 0.18 wt% Fe, 0.09 wt% O, and balanced Zr) substrates for deposition of zirconium-silicide coatings were prepared by sectioning square samples 12.7 × 12.7 mm^2, 2.8 mm thick in dimensions. The samples were then ground successively with 320 grit and 600 grit SiC abrasive paper followed by cleaning with acetone and methanol. Three compositions of zirconium-silicide sputter targets (i.e., Zr_2Si, ZrSi, and $ZrSi_2$) were procured from a commercial vendor. The sputter targets were 76 mm in diameter and 3.2 mm in thickness. The targets were of 99.5% nominal purity and with 3.2 mm thick copper backing plates for enhancing thermal conductivity during the deposition process.

Prior to initiating the coating deposition process in the magnetron sputter system, the substrates were subjected to in-situ plasma cleaning (dc 500 W for 5 min under 1.6 Pa argon pressure) to remove any residual surface contamination and native oxide layer on the surface of the substrate. Zirconium-silicide coating deposition was performed using a base pressure of 2.6×10^{-4} Pa. Argon sputter gas pressures were 0.53 Pa and 1.33 Pa with a flow rate of 20 sccm - these parameters were selected based on previous studies of magnetron sputter deposited coatings for high-temperature oxidation resistance [11,12]. DC sputter power was 138 W. The distance between the sputter target and the sample stage was 150 mm and the sample stage was rotated at 10 rpm during the deposition to achieve improved uniformity of the coating. The deposition was performed at 19 °C, as monitored in situ by thermocouples, in order to avoid any phase transformations and thermal stresses in the coatings. In order to investigate the effect of argon pressure and composition of coating on oxidation resistance, the depositions were performed under conditions listed in Table 1. The coating deposition for a single step took 150 min, and six steps were performed to achieve thicker coatings that were also investigated in this study. For this multiple step deposition, a plasma cleaning step was employed between the steps to remove any contamination due to interruptions in the coating process. In addition to Zirc-4 substrates, the coatings were also deposited on plasma cleaned Si (100) wafers, which were used for measuring film thickness and observing coating cross-sectional microstructure.

Isothermal oxidation tests were performed at elevated temperatures in a commercial furnace (e.g., Lindberg box furnace, model#51442). Initial studies involved oxidation tests at 700 °C in ambient air for exposure durations of up to 5 h, with samples being removed each hour for weight change measurements (as an initial measure of the extent of oxidation) performed with Satorius micro-precision balance (model#CPA26P) with 0.002 mg resolution. Annealing of the coatings was carried out in argon environment to understand high temperature stability, which then was used to optimize the multi-step thicker coatings. For this, the samples were encapsulated in argon back-filled quartz tube along with pure zirconium granules to reduce residual oxygen gas during annealing. The thicker coatings produced by multiple tests were tested for oxidation at 700 °C for 20 h, at 1000 °C for 1 h, and 1200 °C for 10 min. Table 1 summarizes the salient features of this experimental study.

Surface morphologies and cross sectional microstructure of the as-deposited, oxidized, and annealed zirconium-silicide coatings were characterized by Zeiss LEO Scanning Electron Microscope (SEM) in conjunction with Energy Dispersive Analysis System (EDS). Phase identification of the coatings was conducted using Bruker D8 Discovery X-ray diffraction (XRD) system with Cu Kα radiation. Diffraction peaks were acquired from 30° to 90° with coupled 2θ mode and from 30° to 50° in 2θ with a 2° grazing incident beam. To identify phases in the as-deposited coatings, thin foils of the coatings were prepared by a Zeiss Auriga Focus Ion Beam milling and imaged with a Tecnai 12 Transmission Electron Microscope (TEM). Very near-surface composition and chemical bonding of phases was evaluated by Thermo-Scientific Kα X-ray Photoemission Spectroscopy (XPS). Prior to the binding energy acquisition, surface cleaning was performed by 3 keV Ar ion source for 30 s under high vacuum to remove any residual surface contamination.

3. Results and discussion

3.1. As-deposited thin coatings

Elemental composition of the very near surface of the as-deposited coatings, as analyzed by the XPS, was consistent in trend with the corresponding target chemistry. Argon gas pressure during the process did not influence the coating composition. Grazing incident XRD patterns showed only peaks corresponding to zirconium from the underlying substrate and no peaks corresponding to the coatings was observed for any of the coating stoichiometries (Fig. 1).

Surface morphology and cross sectional microstructure of the coatings, were investigated using SEM. The coatings showed uniform and smooth surface with no indication of spallation. No noticeable differences in surface topography and microstructure were identified in coatings deposited using the different target compositions. On the other hand, argon gas pressure influenced microstructure significantly as shown for example for $ZrSi_2$ in Fig. 2. The $ZrSi_2$#1 coating deposited at higher argon pressure (i.e., 1.33 Pa) exhibited relatively rougher surface and showed nanometer scale gaps in the microstructure (Fig. 2a). Cross-sectional fracture surfaces of these coatings deposited on Si substrate showed tapered columnar microstructures which are revealed more clearly in Fig. 2c. In contrast, the lower argon pressure (i.e., 0.53 Pa), $ZrSi_2$#2 coating, exhibited short and dense columnar structures with smoother surface, which are shown in Fig. 2b and d. The observation is in good agreement with Thornton's model [13,14] suggesting that the columnar tapered morphology of the films is a result of atomic shadowing and a low mobility of sputtered atoms on the growing surface at low temperatures. In addition, this morphology would be promoted by increased scattering between argon atoms and target atoms at higher argon pressures. It is expected that the nanoscale gaps

Table 1
Summary of zirconium silicide coatings deposited and investigated in this study.

Sample ID	Target composition	Ar pressure (Pa)	Deposition rate (nm/min)	# of steps	Experimental conditions
Zr_2Si#1	Zr_2Si	1.33	6.12	1	700 °C air for 5 h
ZrSi#1	ZrSi	1.33	5.81	1	700 °C air for 5 h
$ZrSi_2$#1	$ZrSi_2$	1.33	5.39	1	700 °C air for 5 h
Zr_2Si#2	Zr_2Si	0.53	5.30	1	700 °C air for 5 h 700 °C Ar for 5 h
ZrSi#2	ZrSi	0.53	4.97	1	700 °C air for 5 h 700 °C Ar for 5 h
$ZrSi_2$#2	$ZrSi_2$	0.53	4.80	1	700 °C air for 5 h 700 °C Ar for 5 h
$ZrSi_2$#3	$ZrSi_2$	0.53	4.80	6	700 °C air for 20 h 1000 °C air for 1 h 1200 °C air for 10 min