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Synthesis of $Zr_2Al_3C_4$ coatings on zirconium-alloy substrates with Al-C/Si interlayers as diffusion barriers

Jiamin Liang^{a,b}, Qiang Wei^{a,c}, Fangfang Ge^b, Donglou Ren^b, Ji Wang^b, Yue Dong^b, Per Eklund^d,
Feng Huang^{*b}, Shiyu Du^b, Qing Huang^{**b}

a. Tianjin key Laboratory of Composite and Functional materials, School of Materials Science and Engineering, Tianjin University, 300350 Tianjin, P. R. China.

b. Engineering Laboratory of Nuclear Energy Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 315201 Ningbo, P. R. China

c. School of Mechanical Engineering, Hebei University of Technology, 300130 Tianjin, P. R. China

d. Thin Film Physics Division, Dept. of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83, Linköping, Sweden

*Corresponding author: huangfeng@nimte.ac.cn

**Corresponding author: huangqing@nimte.ac.cn

Abstract:

$Zr_2Al_3C_4$ coatings are potential candidates to prevent claddings of traditional Zr-based alloys from severe oxidation in water steam at high temperature. However, the diffusion of aluminum between coating and substrates at high temperature results in a coating composition deviating from the compositional domain for formation of the $Zr_2Al_3C_4$ phase. Thus, synthesis of $Zr_2Al_3C_4$ coatings on zirconium-alloy substrates is challenging. Here, we report that the $Zr_2Al_3C_4$ phase can be obtained on zirconium alloy (ZIRLO) substrates where an Al-C/Si interlayer deposited by magnetron sputtering is introduced. The Al-C/Si interlayer prevented elemental diffusion of aluminum between the Zr-Al-C coating and the substrates during a

26 post-annealing process at 800 °C for 3h. The Al/Zr ratio of the Zr-Al-C coating after
27 annealing was ~0.96 and ~0.59 in the cases of with and without Al-C/Si interlayer,
28 respectively. Hence, the Al-C/Si interlayer acts as diffusion barrier and greatly
29 decreases the deviation from the standard stoichiometric ratio of the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase,
30 which facilitates the formation of the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase in the final coating.

31 **Key word:** $\text{Zr}_2\text{Al}_3\text{C}_4$, Coating, interlayer, Diffusion

32

1. Introduction

It is important to enhance accident tolerance of traditional Zr-based alloys for future high-safety reactors, because Zr-based alloys easily react with high-temperature steams. This reaction releases a large amount of hydrogen and can cause explosions, as in the Fukushima nuclear accident [1, 2]. One strategy for the accident-tolerant fuels is to deposit ceramic coatings on the Zr-based alloys to improve the corrosion resistance of the Zr alloys, which doesn't adversely affect the nuclear material criteria [3, 4]. $M_{n+1}AX_n$ (abbreviated as MAX, where M is an early transition metal, A is an IIIA- or IVA-group element, and X is C or N) phase coatings are considered as potential protective coatings for the Zr-based alloy, due to their exceptional properties, combining the merits of metals and ceramics[5]. Among, $Zr_2Al_3C_4$ that is a Zr-based and Al-rich MAX phase ($P6_3/mmc$ space group, $a=b=3.34 \text{ \AA}$ $c=22.2 \text{ \AA}$) [6, 7], would be expected to have better compatibility with the Zr alloys and better oxidation resistance. He *et al.* investigated the oxidation behavior of $Zr_2Al_3C_4$ bulk at 1600 °C and 1750 °C, and found that the formed scales are intact and strongly bonded with the substrate below the eutectic temperature of Al_2O_3/ZrO_2 [8]. Moreover, it was reported that $Zr_2Al_3C_4$ ceramics exhibit good high-temperature mechanical properties. At 1400 °C, the remaining strength of the $Zr_2Al_3C_4$ ceramics is 287 MPa, which is about 77% of that at room temperature. [9].

However, less studies have been performed on the synthesis of $Zr_2Al_3C_4$ coatings. Lai *et al.* deposited epitaxial $Zr_2Al_3C_4$ films onto $\alpha-Al_2O_3$ (0001) and 4H-SiC (001) substrates [10]. In contrast, it is much more difficult to deposit the $Zr_2Al_3C_4$ coatings

on the Zr alloys than that on the single crystal substrates. Firstly, the primary challenge is deviation from stoichiometry caused by the coating-substrate inter-diffusion at high temperatures. As indicated in the phase diagram of Zr-Al-C at 600 °C, many Zr-Al intermetallic compounds (e.g. ZrAl_3 , ZrAl_2 , Zr_2Al_3 , Zr_3Al) exist in balance with the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase [11], which is thermodynamically stable in the triangular zone with end phases of $\text{Zr}_2\text{Al}_3\text{C}_5$, $\text{Zr}_3\text{Al}_3\text{C}_5$ and ZrAl_3 . A stoichiometric ratio (i.e., 2:3:4) of the three elements (Zr, Al, C) is a prerequisite for the synthesis of the pure $\text{Zr}_2\text{Al}_3\text{C}_4$ phase. Deviations from stoichiometry can result in impurity phases, and typically occurs during annealing at high temperature, due to significant inter-diffusion between the coating and substrate. Secondly, another concern is mismatches in the lattices and the thermal expansion coefficients between the $\text{Zr}_2\text{Al}_3\text{C}_4$ coating and the substrates. The lattice mismatch ($\sim 3.37\%$) and their different thermal expansion coefficients ($8.1 \times 10^{-6} \text{ K}^{-1}$ for the $\text{Zr}_2\text{Al}_3\text{C}_4$ and $7.2 \times 10^{-6} \text{ K}^{-1}$ for the ZIRLO zirconium alloy) could affect the coating-substrate adhesion [10, 12]. We would prefer to use interlayers for reducing the mismatches between the $\text{Zr}_2\text{Al}_3\text{C}_4$ coatings and the Zr-alloy substrates.

Here, we reported the synthesis of $\text{Zr}_2\text{Al}_3\text{C}_4$ coatings on Zr-alloy substrates (ZIRLO) by introducing a magnetron-sputter-deposited interlayer of Al-C/Si acting as diffusion barrier during post-annealing.

2. Experimental details

A Zr-Al-C coating with a Al-C/Si interlayer (i.e. Zr-Al-C/Al-C/Si) and a Zr-Al-C

77 coating without any interlayers were deposited at room temperature (without ambient
78 heating), by using a magnetron sputtering system (KYZK Development Co. Ltd,
79 China), respectively. The plates of ZIRLO (State Nuclear Bao Ti Zirconium industry
80 Co. Ltd, China) with the size of 15 mm × 15 mm × 1 mm were chosen as the
81 substrates. The nominal composition (wt.%) of ZIRLO is given as follows Zr bal;
82 Nb,1.10; Sn,1.10; Fe,0.11; O,0.13. After being polished to 3000-grit and then polished
83 to mirror with diamond polishing paste, the substrates were ultrasonically cleaned in
84 acetone and ethanol each for 10 min, blown dry in N₂ gas, and immediately loaded
85 into an ultrahigh-vacuum magnetron sputtering system. During the deposition process,
86 four targets (diameter 100 mm, thickness 4 mm, 99.99 at. % in purity, ZNXC
87 Technology Co., Ltd) of Zr₂Al, Al, graphite, and Si were driven by the direct current
88 (dc) powers; and the powers was 150 W, 42 W, 100 W and 450 W, respectively. All
89 the depositions were performed in Ar discharges at a pressure of 0.5 Pa, with a
90 substrate dc bias of -15 V. Before deposition, the chamber was evacuated to a pressure
91 of approximate 2×10^{-4} Pa. The targets were pre-sputtered for at least 10 min.
92 Subsequently, the as-deposited samples were isothermally annealed at 800 °C for 3 h
93 in vacuum, using a furnace (KYZK Development Co. Ltd, China). The 800 °C was
94 selected for the annealing, because the Zr alloys generally proceed phase transition
95 when the temperatures are more than 860 °C. Prior to the annealing, the chamber was
96 pumped down to 2.0×10^{-3} Pa. Both the heating and the cooling rates were fixed at
97 5 °C/min. Phase identification was performed by X-ray diffraction (XRD) on a Bruker
98 D8 Advance diffractometer, and Raman spectroscopy on a LABRAM-HR system

with the excitation laser of 532 nm. Cross-sectional microstructures were examined by a field emission scanning electron microscope (SEM, FEI Quanta FEG 250) and transmission electron microscopy (TEM) on a FEI Tecnai F20 system operated at an acceleration voltage of 200 kV. An energy dispersive X-Ray spectroscopy (Oxford Instruments X-MAX 50) was used to determine the compositional profiles. The quantification was conducted using the XPP method and system build-in database. A focused ion beam (FIB) microscope (Auriga, Carl Zeiss) was used to prepare the cross-sectional TEM specimen. First, a rectangular region of $7\ \mu\text{m} \times 10\ \mu\text{m}$ was selected on the surface of the sample, and the Ga ion beams were used to bombard a rectangular region with the depth of $5\ \mu\text{m}$. Then the sides of the cross-section sample were thinned by the focused ion beam. The sample was thinned to about 500 nm at the voltage of 30 kV and the current of 4 nA - 2 nA, and was further thinned from 500 nm to 100 nm at the voltage of 5 kV and the current of 130 pA - 20 pA.

3. Results and discussion

Fig. 1 shows SEM images of the cross-section morphologies of the as-deposited coatings on the ZIRLO substrates, one for the Zr-Al-C coating without interlayer and another one with the Al-C/Si interlayer. The elemental compositions of the deposited Zr-Al-C layers are identical in these two cases, with the atomic ratio of Zr: Al: C is 30.3: 47.3: 22.4. In Fig. 1a the coating only contains a dense and uniform Zr-Al-C layer with a thickness of $\sim 1.8\ \mu\text{m}$. There are three layers on the substrates in Fig. 1b, corresponding to an identical Zr-Al-C layer, a 150 nm thick Al-C interlayer, and a 200

nm thick Si layer, respectively. The atomic ratio of Al: C is 37.7: 62.3 in the Al-C interlayer.

XRD patterns and Raman spectra of the as-deposited coatings are presented in Fig. 2. The two as-deposited coatings exhibit similar XRD patterns and Raman spectra. Only the diffraction peaks of the ZIRLO substrates were detected. The characteristic peaks of the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase could be distinguished neither in the XRD patterns nor in the Raman spectra, which might suggest that the as-deposited coatings composed of amorphous phase, and the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase did not form at the room temperature.

After the 800 °C annealing, the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase did not appear in the interlayer-absent coating yet. In Fig. 2a, there is not any diffraction peaks of (002) plane for the $\text{Zr}_2\text{Al}_3\text{C}_4$ MAX phase at $\sim 7.9^\circ$, maybe indicative of an absence of the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase, since the low-angle diffraction peaks are the characteristic peaks of the MAX phases [13, 14]. The diffraction peaks in Fig. 2a, such as 33.2° , 37.5° , 39.5° , 55.5° , 60.5° , and 65.5° , might come from the $\text{Zr}_3\text{Al}_3\text{C}_5$ or the ZrAl_3 . In the Raman spectrum (Fig. 2b), the Raman peaks at $\omega=178, 544 \text{ cm}^{-1}$ correspond the Raman active modes of ZrC, and the peaks at $\omega=1335, 1580 \text{ cm}^{-1}$ are the so-called D and G bands of amorphous carbon [15]. But no distinct Raman peaks for the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase were detected. Based on the absences of the diffraction peak of (002) plane and the characteristic Raman peaks, we preferred to suggest that the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase might not form in the single-layer coating after the annealing.

However, the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase formed in the coating with the Al-C/Si interlayer

after annealing at 800 °C for 3h, as demonstrated in the XRD pattern and the Raman spectrum of the annealed coating in Fig. 2c and Fig. 2d. Particularly, the typical diffraction peak at 7.9° that originates from diffraction at the (002) planes of $\text{Zr}_2\text{Al}_3\text{C}_4$ MAX phase [10, 16], was detected in the XRD pattern (Fig. 2c). The Raman peaks at $\omega=111, 177, 258, 414, \text{ and } 625 \text{ cm}^{-1}$ can also be assigned to the distinct Raman active-modes of $\text{Zr}_2\text{Al}_3\text{C}_4$ [17]. Besides the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase, the ZrAl_3 and the $\text{Zr}_3\text{Al}_3\text{C}_5$ phases were also contained in the annealed coating. Their corresponding characteristic peaks appear in the XRD pattern, and the Raman peaks in Fig. 2d at $\omega=325, 537, 583 \text{ cm}^{-1}$ could be attributed to the corresponding active modes of $\text{Zr}_3\text{Al}_3\text{C}_5$ [18]. Moreover, the percentages of the phases, estimated from the strongest peaks of individual phase by the internal standard method, are 51.3%, 40.9%, 7.8% for the $\text{Zr}_2\text{Al}_3\text{C}_4$, the $\text{Zr}_3\text{Al}_3\text{C}_5$ and the ZrAl_3 , respectively. In the preparation process of bulk $\text{Zr}_2\text{Al}_3\text{C}_4$, the $\text{Zr}_2\text{Al}_3\text{C}_4$ and the $\text{Zr}_3\text{Al}_3\text{C}_5$ phases simultaneously appeared above 1160 °C, while the ZrAl_3 phase dominates in lower temperature ranges [16]. According to the results of XRD and Raman, it could be concluded that the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase was obtained by annealing of the coating with the Al-C/Si interlayer, but did not form in the annealed single-layer Zr-Al-C coating.

Fig. 3 shows cross-sectional TEM images of the annealed Zr-Al-C/Al-C/Si coating. In a low-magnification image (Fig. 3a), three distinct layers are stacked in sequence, namely the Zr-Al-C layer, the interlayer, and the substrate. The interlayer is ~100 nm in thickness, becoming thinner than that of the as-deposited one (~350 nm), which could be attributable to composition homogenization due to the interdiffusion

between the Zr-Al-C layer and the interlayer in the annealing process. In Fig. 3b, the selected-area electron diffraction pattern (SAED) that was taken from the Zr-Al-C layer, consists of rings mixed with several spots, indicative of random orientation. Consistently in a high-resolution TEM image (Fig. 3c), there are some nanosized grains, with the sizes of 5-10 nm. Also apparent was that the grains with the large lattice distances >5 Å could be considered the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase, especially the lattice distance of ~ 11.1 Å that represents its (002) plane. Therefore, it could be confirmed that the nanosized $\text{Zr}_2\text{Al}_3\text{C}_4$ crystal grains were contained in the Zr-Al-C/Al-C/Si coating after the annealing treatment.

To better understand the mechanism of the formation of the $\text{Zr}_2\text{Al}_3\text{C}_4$ phase in the Zr-Al-C/Al-C/Si coating after the 800 °C annealing, we compared the cross-sectional SEM images and their corresponding EDS profiles between the single-layer coating and the coating with the Al-C/Si interlayer. In Fig. 4, overall the cross-sectional morphologies of the annealed coatings are different from those of the as-deposited ones (Fig. 1), maybe due to composition diffusion and phase formation occurred in the annealing processes. Fig. 4a shows that a compositional diffusion is predominant during the annealing process of the single-layer coating. The diffusion might be mainly considered as the Al atoms towards the Zr substrate, since the solubility limit of Al in Zr (1.2 at.%) is ~ 17 times as much as that of Zr in Al (0.07 at.%) at the 838-898 K temperature [19]. The Al atoms diffused towards the substrate, resulting into the formation of a 2 – 2.5 μm thick Al-Zr mixed zone. The content of the Zr gradually decreases from the bottom of the coating to the surface. Such

compositional diffusion was observed for V_2AlC thin films [20]. However, the inter-diffusion of Al and Zr was impeded in the sample with Al-C/Si interlayer, as Fig. 4b shows. The Zr content in the coating is almost constant over the whole thickness and is substantially lower than that in the substrate, indicative of a relatively uniform distribution of the Zr composition in the coating. By contrast, the content of the Al composition is much higher in the coating than that in the Zr substrate; and the diffusion depth of the Al atoms into the substrate decreases to $1.5\sim 2\ \mu\text{m}$. Instead, an aggregation zone of Si of $\sim 700\ \text{nm}$ also formed in the surface/subsurface of the ZIRLO alloy substrate.

The chemical compositions of the as-deposited samples and the annealed samples are summarized in Table 1. The two as-deposited Zr-Al-C layers have an Al/Zr ratio of ~ 1.56 . The Al/Zr ratio decreases after the annealing treatment to ~ 0.59 and ~ 0.96 for the samples without and with the Al-C/Si interlayer, respectively. The compositions in Table 1 thus supports the interpretation that the inter-diffusion of the Al and the Zr atoms was reduced by the added Al-C/Si interlayer. Additionally, the Al-C sub-interlayer could partly compensate for the loss of Al during annealing, and reduce the deviation from the stoichiometric ratio of the $Zr_2Al_3C_4$ phase.

According to the Zr-Al-C ternary phase diagram [11], the Al/Zr ratio of ~ 0.59 is far from the stoichiometric ratio of the $Zr_2Al_3C_4$ phase, and belongs to the three-phase region of C, ZrC and $Zr_2Al_3C_5$. Thus, it seemed reasonable that the ZrC and the amorphous carbon, instead of the $Zr_2Al_3C_4$ phase, existed in the single-layer sample after the annealing. However, the Al/Zr ratio of ~ 0.96 is in the three-phase region of

ZrAl₃, Zr₂Al₃C₅ and Zr₃Al₃C₅, being consistent with the observations that the three phases were present in the sample with the Al-C/Si interlayer. Based on the results above, we proposed that the Al-C/Si interlayer can reduce the deviation from the stoichiometry of the Zr-Al-C ternary phase that usually occurs in the coatings on Zr-alloy substrates at high-temperature. Finally, it is worth to point out two main problems in this work. The annealing temperature and the annealing time are required to be further lower, otherwise the Zr substrates will be damaged at the high temperature annealing for the long time. Moreover, the coatings were not suitable in practice application yet, as the low purity (~51.3%) of the Zr₂Al₃C₄ MAX phase and the random orientations could result into swelling and cracking of the coatings upon neutron irradiation. Therefore, in the future work, we plan to optimize the Al-C/Si interlayer or design other interlayers, such as Al₂O₃. In addition, we are also going to use our one-step synthesis, by which we have obtained phase-pure V₂AlC MAX phase films at 600 °C on amorphous substrates [21].

4. Conclusions

Zr₂Al₃C₄ phase on ZIRLO substrates can be obtained in magnetron sputtered Zr-Al-C coatings by adding an Al-C/Si interlayer between the Zr-Al-C layer and the substrate, followed by annealing at 800 °C for 3h. The Al-C/Si interlayer can impede inter-diffusion of the Al and the Zr atoms, and retain the element composition close to the stoichiometry of Zr₂Al₃C₄ phase, which helps the formation of Zr₂Al₃C₄ phase.

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Fig. 1. Cross-sectional morphology of the as-deposited Zr-Al-C coatings on the ZIRLO alloy substrates (a) without interlayers, and (b) with a Al-C/Si interlayer.

Fig. 2. XRD patterns and Raman spectra of the as-deposited and annealed samples. (a) and (b) for the sample without interlayer. (c) and (d) for the sample with the Al-C/Si interlayer. The background of the XRD patterns was removed. The range of peak positions taken from JCPDF card #78-1801, #65-5706, #70-2655 and #05-0665.

Fig. 3. TEM cross-section images of the annealed Zr-Al-C/Al-C/Si coating on the ZIRLO substrate. (a) An overview image, (b) a selective area electron diffraction (SAED) patterns marked in (a), (c) a HRTEM image showing individual grains outlined by dashed lines

Fig. 4. Cross-sectional SEM images and their corresponding EDS linescans for the annealed samples, (a) the Zr-Al-C coating without interlayer, (b) the coating with the Al-C/Si interlayer

Table 1 Chemical compositions of the as-deposited and the annealed samples by EDS (at %)

Table 1 Chemical compositions of the as-deposited and the annealed samples by EDS (at %)

Element	As-deposited Zr-Al-C	Annealed Zr-Al-C coating	
		Without interlayer	With interlayer
Zr	30.3	28.3	27.6
Al	47.3	16.8	26.6
Al/Zr	1.56	0.59	0.96

Highlight

- 1, the interlayer barrier is crucial to inhibit the inter-diffusion of elements between Zr substrate and $\text{Zr}_2\text{Al}_3\text{C}_4$ coating;
- 2, $\text{Zr}_2\text{Al}_3\text{C}_4$ coatings are successfully synthesized on zirconium-alloy that will be a promising candidates as accident tolerant fuel cladding.