Laser Surface Annealing and Characterization of Ti_2AlC Plasma Vapor Deposition Coating on Zirconium-alloy Substrate

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Abstract

Laser surface treatment of amorphous Ti-Al-C (50:25:25 at.%) coating deposited on Zircaloy-4 substrate by dc magnetron sputtering was parametrically investigated as a function of surface temperature and dwell time. The as-deposited coating was transformed to crystalline Ti_2AlC without significant phase alteration of Zircaloy-4 substrate under optimized conditions (900 °C for 3 second). [Thermal analysis via commercial finite element software](#) was applied to guide the selection of parameters for laser surface treatment. Coating performance was evaluated with wear and scratch tests as well as high temperature steam oxidation tests. Although laser treatment led to the formation of microcracks, it was noted to improve the mechanical integrity of the coatings and the oxidation tests indicated the protective nature of the as-deposited and laser-annealed coatings. The oxide particulate morphology and size formed during the steam oxidation tests varied dramatically between the as-deposited and laser-annealed coatings.

KEYWORDS

Ti_2AlC Maxphase

Magnetron Sputter Deposition

Laser Surface Annealing

Wear Test

High Temperature Corrosion Test

1. Introduction

In a loss of coolant accident, the zirconium-alloy fuel cladding in light water reactors (LWR) can heat up to high temperatures (in excess of 1000 °C) and reacts with steam via a highly exothermic oxidation reaction and lose its mechanical integrity. This reaction is also accompanied by evolution of hydrogen. Without a quick restoration of cooling, cladding failure will follow allowing the release of radioactive materials from inside the fuel cladding to the environment. Deposition of oxidation-resistant coating on Zirconium-alloy cladding may offer a potential near-term solution to such rare but serious accidents. There have been a number of studies that have investigated coatings for enhancing oxidation resistance of materials in general. For example, Titanium-nitride film using pulsed laser deposition on stainless steel bars [1], molybdenum-disilicide coating using high velocity oxyfuel process on carbon steel substrate [2], and chromium coating by reactive radio frequency magnetron sputtering on low carbon steel [3] have all been investigated with varying levels of success. Relatively few studies have been performed on using thin coatings as anti-oxidation layers for Zr-alloy substrates [4]. One possible reason for this is that many of the surface treatments are performed at high temperatures or require high temperature post-deposition treatments which adversely affects the critically heat-treated microstructure of the Zr-alloy [4–6] for LWR fuel cladding. Due to microstructure-specific properties of the Zr-alloys, the substrate temperature must be maintained at temperatures below 850 °C to prevent phase transformation [7], but from a practical stand-point, for fuel cladding application, it is recommended that the temperature not exceed 500 °C for a long period of time.

One approach is to deposit protective films on the Zr-alloy surface at relatively low temperatures followed by near-surface heat treatment of the coating that would minimize

alteration of the underlying Zr-alloy. In this regard, laser beams are quite effective in delivering a tailored amount of energy into a limited volume of material for a short time. For example, R. Krishnan et al. [8] demonstrated the transformation of metastable γ -Al₂O₃ deposited by air plasma spray to stable α -Al₂O₃ using continuous-wave CO₂ laser irradiation. C. Demian et al. [9] conducted diode laser treatment on an organic coating (polyetheretherketone), and achieved porosity reductions with various laser parameters.

In the present study we report results of our investigation of laser surface annealing effects on Ti-Al-C (50:25:25 at.%) coating on Zircaloy-4 (referred to henceforth as Zry-4) substrate, deposited by magnetron sputtering, and ensuing structure and property evaluation. This stoichiometry corresponds to Ti₂AlC MAX (M_{n+1}AX_n) phase composition which is known for its high thermal conductivity and thermal shock tolerance, and excellent oxidation resistance due to the formation of Al₂O₃ on the surface at high temperatures[10–12]. The material was therefore deemed to be a potential candidate coating for protection of Zry-4 against high temperature oxidation.

2. Experimental Details

2.1. Ti₂AlC coating fabrication

Ti₂AlC coatings were deposited on Zry-4 test flats (31.7 mm x 12.7 mm and 3.2 mm) using the plasma vapor deposition (PVD) at Savannah River National Laboratory (SRNL). Prior to deposition, the samples were ground progressively with 320 grit and 600 grit silicon-carbide abrasive paper followed by cleaning with methanol, and finally cleaning in a Plasma-Preen system.

The deposition was performed by magnetron sputtering using a Kurt J. Lesker system using three circular elemental targets (50.8 mm in diameter and 6.35 mm in thickness): Ti (99.995%), Al (99.9995%) and C graphite (99.999%), operated in constant current mode and individually controlled with an Advanced Energy MDX 500 power supply. The magnetron cathodes had tilt angles of approximately 15 ° with respect to the substrate's normal and are located at 120 ° from each other as viewed from top. Batches of two or three substrates were placed on the stage, located at the center of the chamber and 9.5 cm below the targets. The stage was rotated at 12 rotations per minute. The vacuum chamber had a base pressure of 10^{-7} Pa and sputtering was performed with argon gas at a pressure of 0.5 Pa and at room temperature.

Initial calibration tests were performed on Si wafers to allow calculation of the sputtering rate and adjustment of the current to be set to each target in order to achieve the desired coating composition. These sputtering parameters were then used to achieve a stoichiometric ternary compound (Ti_2AlC) by simultaneous deposition of the three components. Between batches, some adjustments to the current were necessary in order to maintain consistent stoichiometry. Hence, the range of current used between batches were 450-650 mA for Ti, 180-200 mA for Al, and 215-250 mA for C. Prior to sputtering the Ti_2AlC coating, a Ti seed layer followed by a TiC seed layer were deposited on the Zry-4 alloy surface to improve the coating adhesion. The thickness of the seed layers was on the order of 10 nm. The composition of the as-deposited Ti-Al-C coatings, their respective thicknesses, and the tests employed for each sample is summarized in Table 1.

2.2. Laser surface treatment

Laser surface treatment of as-deposited Ti-Al-C samples was performed at PRECO Inc., a company specializing in laser processes. Preliminary laser surface treatment utilized an

integrating lens to produce a rectangular 3 x 6 mm spot with a spatially normalized power distribution. The trial temperatures ranged from 700-1100 °C, with surface dwell times of either 1 or 3 seconds. Previous studies have shown that phase transformations including amorphous to crystalline phase transformation can be induced in the temperature range of 800-850 °C [6,13]. Due to the capabilities of laser equipment and a simple approximation of Al self-diffusion at 800 °C a dwell time on the order of one second was set. The 1.07 μm fiber laser (IPG 6kW laser) output was controlled with an optical pyrometer ([a fiber coupled two color pyrometer QP004](#)) and [a Proportional-Integral-Derivative \(PID\)](#) controller to achieve and maintain a target temperature. Argon was used as the cover gas to reduce oxidation of the sample, and the sample was placed on an aluminum fixture to increase the rate of heat transport out of the sample. The laser surface heating conditions and corresponding result are shown in Figure 1a and 1b.

Following observations from above preliminary studies, a second laser treatment was employed using a continuously-rastered laser with the optimized parameters (i.e., 900 °C for 3 second dwell time). The laser spot was oriented with the 3 mm geometry parallel to the direction of travel, and the feed rate was set to 1 mm/second to achieve a 3-second dwell time. Figure 1c shows the surface of the coating produced by optimal conditions of laser rastering.

2.3. Coating Characterization and Testing

2.3.1. Coating Surface Characterization

Surface morphology and cross-sectional observations of as-deposited and laser-treated Ti-Al-C coatings were carried out by a Zeiss LEO [Scanning Electron Microscope \(SEM\)](#). Phase identification of the coatings was conducted by Bruker D8 Discovery X-ray diffraction system with Cu K α radiation and diffraction peaks were acquired from 30° to 90° in 2 θ . Specific laser treated samples were also examined in cross-section by using a 1540XB CrossBeam Focused Ion

Beam SEM (FIB) to get a clearer image of the coating structure from the top of the coating to the coating-substrate interface.

2.3.2. Wear Testing

Wear testing of as-deposited and laser-treated coatings was conducted with a pin-on-disc wear tester. Using a 3 mm diameter ruby ball (Al_2O_3) stylus under an impressed force of 98 mN with the sample table was rotating at 143 rpm for 120 min. A 3-5 mm diameter circular wear track formed on the sample as a result of the wear tests and the relative wear performance was characterized by measurement of the average width of wear track. Scratch testing was carried out as an additional check of the coatings' mechanical integrity. A standard Rockwell indenter (20° cone with 0.2 mm radius) was slowly traversed across the coated surface under a force of 2.5 N with the speed of 15 mm/min to make a controlled scratch on the coating surface.

The width of the wear track and scratch were measured using SEM, and coating penetration was evaluated by examining x-ray elemental maps for substrate elements. Elemental maps were prepared using the Noran System six Energy-Dispersive X-ray Spectroscopy (EDS) software. The accelerating voltage and working distance for the EDS analysis was 12 kV and 15 mm, respectively. The wear track width, presence/absence of complete coating penetration, and scratch width were used as criteria for the evaluation of mechanical properties of the coatings.

2.3.3. Autoclave test

A high-temperature water/steam autoclave 4 cm (1.6") dia. x 50.8 cm (20") long was used to test the corrosion of the coated samples at 400 °C and 10.3 MPa (under these conditions the environment is steam). The test section was made of nickel alloy 625 and it is capable of operating at maximum temperature and pressure of 650 °C and 35 MPa, respectively. The minimum measurable dissolved oxygen is 3 ppb. The variation of the temperature and pressure

in the sample test section are ± 1 °C and ± 0.2 MPa, respectively. For the purposes of this study, the samples were mounted onto a holder, also made of Alloy 625, with electrical isolation being achieved by using alumina washers between the samples and sample holder.

3. Results and Discussion

3.1. As-Deposited PVD coating

The surface morphology of Ti-Al-C coated samples was typical fine bulbous grain structure, and its grain size is approximately 0.3-1 μm as shown in Figure 2 (a) and (b). No significant defects were observed and the general directionality of the grain structure appeared to scratches of the underlying substrate (underlying substrate was ground to 600 grit as final step).

X-ray diffraction studies showed peaks predominantly corresponding to zirconium from the underlying substrate but an amorphous “hump” corresponding to the coating was observed at a 2θ of about 38° in all coated samples (Figure 2c). The as-deposited Ti-Al-C coatings were not crystalline Ti_2AlC , but rather amorphous in nature presumably due to the low temperature used in the magnetron sputtering process in the present study [14].

3.2. Laser Annealing Optimization

3.2.1. Preliminary Laser Annealing

To optimize the laser annealing parameters of surface temperature and dwell time, observation of the surface morphology and phase identification of the Ti-Al-C coated samples laser-treated under various conditions were performed. For all conditions, the original print-through of substrate topography structure remained and the micron to sub-micron scale bulbous grain structure were retained after the laser treatment (Figure 3a). As shown in Figure 3b, large cracks were observed across grain boundaries even under the mildest conditions while spallation

was not observed even at the harshest condition. The stresses from rapid heating and cooling on the small area during the static laser treatment are assumed to be one of causes of cracking. No significant visual microstructural changes were observed in all laser heating conditions.

Phase transformation of Ti-Al-C coating during the laser surface treatment was investigated using X-ray diffraction (XRD) at room temperature. Figure 4 summarizes the XRD peaks for uncoated Zry-4 substrate, as-deposited condition, and laser-treated regions subjected five temperatures for dwell time of 3 seconds. Peaks associated with zirconium are unmarked, while circles and crosses indicate Ti_2AlC peaks and other phases (e.g., TiAl), respectively. The formation of TiAl was reported as an intermediate phase or impurity of Ti_2AlC ceramic [15]. At the 700 °C treatment temperature, no observable phase changes were found to occur. At 800 °C, the amorphous hump associated with Ti-Al-C, near 38°, begins sharpening, indicating the onset of crystallization of amorphous Ti_2AlC . At 900 °C, additional Ti_2AlC peaks develop with the largest peak identified at 39.5°. The relative intensities of the Zr peaks and their shape remained unaltered indicating the microstructure of the substrate is not measurably affected by the laser treatment. At 1000 °C and higher treatment temperatures, enough energy is available to both crystallize the Ti_2AlC phase and form detectable amounts of additional phases. The presence of these additional peaks (for example, at 44° and 45°) was also observed in the 900 °C treatments, but their intensity was considerably weaker. At these high laser treatment temperatures, the intensity and shape of the Zr substrate peaks changes, implying undesirable changes of the texture of near-surface Zry-4 substrate (i.e., phase transformation from α phase to β phase [7]). The longer dwell time (3s) improved densification of Ti_2AlC phase in comparison to the shorter dwell time of 1 second. Based on the results of the characterization of the preliminary laser

treated surface, laser heating at 900 °C for 3 seconds was decided to be the best condition for future laser processing.

3.2.2. Estimation of Substrate Effect by Spot Laser Annealing

An attractive feature of laser surface treatment is the theoretical reduction in thermal energy transferred to the bulk material during the heat treatment. The post-treatment XRD characterization indicated that alteration of the substrate peaks in the present study was dependent upon a surface temperature of at least 1000 °C (Figure 4), providing a limitation based on the heat affected zone in the substrate.

An approximate analysis of the effect of laser surface treatment on the substrate is to simulate the transient temperature evolution using numerical calculation. COMSOL Multiphysics (version 4.4) code was used to perform a transient heat conduction analysis for a 5 µm thick Ti₂AlC coating deposited on a 3.2 mm thick zirconium substrate. Figure 5 illustrates the model geometry, a snapshot of the laser heating simulation, and the temperature history on the coating as a function of time. This laser heating model was developed to simulate the actual laser processing but with assumptions discussed below. The simulation used a volumetric heat source inside the coating, as shown in Eq. (1) [16].

$$Q_c(x, y, z) = Q_o(1 - R_c) \frac{A_c}{\pi\sigma_x\sigma_y} \exp\left(-\left[\frac{(x-x_o)^2}{2\sigma_x^2} + \frac{(y-y_o)^2}{2\sigma_y^2}\right]\right) \exp(-A_c z) \quad (1)$$

This source is a 2D Gaussian shape with an exponential decay of heating with increasing depth. The parameters σ_x and σ_y control the effective spot size, while A_c is the absorption coefficient, Q_o is the incident power, and R_c is the reflection coefficient. Due to software limitations, the absorption coefficient of the Ti₂AlC was assumed to be 10^6 , although the actual value may be as high as $\sim 10^7$, as is with many metals [17]. The reflection coefficient was set to

0.63, for a cold rolled 316 stainless steel with a clean surface for a YAG laser ($\lambda=1.053 \mu\text{m}$) irradiation [18]. The model simulated the temperature evolution in the actual length-scale of the substrate. The long axis and short axis of the laser spot were 6 mm and 3 mm, respectively. Feed rate was set to be 1 mm/s, which led to 3 second laser dwell time. Empirical correlation of temperature-dependent thermal properties of Ti_2AlC [12] were used in the calculation, while the software's built-in temperature-dependent properties were used for the zirconium substrate. Initial temperature of the model was room temperature (20°C). A natural convection boundary condition ($h = 20 \text{ W/m}^2$) was used for the coating surface and four of the side surfaces. The bottom of the sample was thermally insulated and radiation heat transfer from this surface was disallowed. The input peak power value was varied to maintain the desired surface temperature (900°C) along with a path of the laser spot. For example, higher laser power (500 W) was required in the initial stages of the process than the power required (120 W) half-way during the process. Lesser energy was required to attain the target temperature while the laser annealing was progressing, resulting from the propagation of the thermal front ahead of the laser spot, as shown in Figure 5a. In addition, the heat is quickly dissipated after the laser spot passes over. Figure 5b shows temperature changes of the top and bottom surfaces in the model at a fixed position ($x = 12 \text{ mm}$ and $y = 0 \text{ mm}$ in Figure 5a). As the laser spot approaches, the surface temperature increases rapidly. After the laser spot passes over the region of treatment on the surface, the temperatures gradually decrease by convective heat removal. Simulation of the laser surface treatment process indicates that the substrate temperature increased above 850°C (the temperature which zirconium undergoes phase transformation [7] only for 7 seconds. Results from this simulation indicate the laser annealing treatment is capable of heating a thin Ti_2AlC coating to 900°C without appreciable thermal damage to the underlying zirconium substrate.

3.2.3. Large-area Laser Annealing

Based on the preliminary characterization results of spot-treated regions, a laser surface treatment of the entire sample surface was performed by rastering a 3 mm x 6 mm rectangular spot of equalized intensity 1 mm/s moving speed and achieving a 900 °C surface temperature using the PID power control and an optical pyrometer. As shown in Figure 6a, during initial heating of the coating, relatively a large amount of radiation power was needed to increase surface temperature from room temperature to the set temperature. After this, the laser power was stabilized while the laser spot was continuously moved on the coating surface by lateral heat diffusion through the sample surface. The trend is consistent with the result of the numerical simulation. The actual stabilized laser power (~210 W) was larger than the simulated laser input power (120 W), which is attributed to increase of convective surface heat transfer enhancement by argon cover gas flow and conductive heat transfer to the aluminum support underneath the flat sample. As shown in XRD results in Figure 6b, the amorphous Ti-Al-C hump was fully converted to sharp peaks of crystalline Ti_2AlC , while the zirconium substrate peaks were not altered. Observation of the coating surface revealed that the continuous laser annealing induced the formation of a network of micro-cracks on the surface as shown in Figure 6c. This microcracking was seen to occur largely along the grain boundaries. However, no spallation or delamination of the coating was observed. A Focused Ion Beam (FIB) SEM was used to image the cross section of these microcracks, and the cracks appear to extend into the substrate, while the substrate-coating bond was free of defects of debonding effects as shown in Figure 6d. It is speculated that crack formation is a result of a combination of thermal shock incurred during the high heating and cooling rates in the coating during laser treatment and the amorphous to crystalline transformation of the coating. It will be discussed again in the later section.

3.3. Performance of Laser-annealed Coating

3.3.1. Wear Tests

The results of the pin-on-disk wear tests performed on the as-deposited and laser annealed coatings are shown in Figure 7. As may be noted in Table 1, these two coatings, sample 4 and sample 8, have very identical stoichiometries and a similar thickness. The average width of the wear track is taken as a measure of wear resistance, with smaller being values being indicative of higher wear resistance. Both as-deposited coatings and laser-annealed coatings protected the substrate during the wear tests; the laser annealed Ti_2AlC and as-deposited coating displayed 77% and 74% wear width reduction compared to uncoated flat Zry-4 substrate, respectively. Figure 7 (a-c) shows images of the wear track on the three samples. As may be seen the wear track is visibly wider for the uncoated Zry-4 compared to the coated samples. Likewise, the wear track width is smaller and more well-defined in width for the laser treated samples compared to the as-deposited coatings. The results of pin-on-disc wear tests were supported by the results of scratch tests, the images for which are shown in Figure 7 (d-f). As may be seen the width of the scratch performed under identical conditions is the highest of uncoated Zry-4 and was smaller for laser surface treated samples compared to the as-deposited samples. No delamination effects were observed indicating that the coatings were well adhered to the substrate. The improvement of wear resistance is in a good agreement with the recent published work. For example, Naveed et al. [19] found that crystalline Ti_2AlC coating (20 μm thickness) provided good protection against high speed solid particle erosion. It is interesting to note that the wear and scratch resistance were enhanced by the laser annealing even though the microcrack extended to the substrate as shown in Figure 6d. This may be attributed to enhanced adhesion between the coating and the substrate by interfacial mixing during the laser annealing.

3.3.2. High Temperature Steam Autoclave Test

The autoclave test in high temperature, high pressure steam environment (400 °C and 10.3 MPa for 72 hours) of the uncoated, as-deposited, and laser-treated samples gave rise to significant changes on the surface, as shown in Figure 8 (a-c). The bare zirconium coupons developed cracks and uneven surface oxidation. A 1-2 μm thick oxide layer was identified on the uncoated sample (Figure 8d). Oxide precipitate particulates were observed on both as-deposited and laser-treated samples but varied dramatically in morphology and size. The oxide particles formed on the as-deposited coating sample were needle-like and polyhedral, while those formed on the laser-treated samples were smaller blocky shapes (see Figure 8b and c). EDS analysis confirmed high oxygen content on each surface. As may be seen from comparing Figure 8d with Figure. 8e and 8f, both as-deposited and laser surface treated coatings protected the substrate effectively from the steam environment. Moreover, localized pockets of ZrO_2 are detected along the coating-substrate interface, and this oxygen ingress correlated with the presence of microcracks in the coating which allowed oxygen permeation. These regions are indicated by the red arrows in Figure 8e and 8f. In the regions where there no microcracks oxygen diffusion through the coatings seems to be greatly reduced indicating that the coatings inherently are protective of the Zry-4 under the conditions of the steam environment in which they were tested.

The phases formed during the ASTM G2 test were identified by XRD (see Figure 9). The uncoated sample contained two distinct phases of zirconia ([monoclinic](#)- ZrO_2 and [tetragonal](#)- ZrO_2) and zirconium. Both as-deposited and laser treated coatings exhibited TiO_2 (anatase) and [monoclinic](#)- ZrO_2 peaks, but the intensities of these oxide peaks in laser-annealed coating was weaker than that of the as-deposited coating. This observation is consistent with SEM surface observations in Figure 8 (fewer oxide particles/less oxide pockets). Partial transformation of

amorphous phase in as-deposited coating into Ti_3AlC during the corrosion test was also observed.

3.4. Formation of Microcracks

It is recognized that the formation of microcracks on Ti_2AlC coatings during laser surface treatment is a concern from the standpoint of corrosion protection, even though it enhanced coating-substrate adhesion, and performance in autoclave tests and wear tests. Postulated mechanisms of the microcrack formation during laser surface treatment, include local thermal shock due to thermal coefficient mismatch between the coating and the substrate, and stress relaxation stemming from crystallization of the Ti_2AlC coating. To provide further insights into the mechanisms of microcracking, the coated samples were annealed in a furnace at 900 °C for 30 minutes with low ramp rate (5 °C/min). Even with this heat treatment which did not involve the rapid temperature excursion, microcracks were identified on the coating. Furthermore, the thermal expansion coefficient of crystalline Ti_2AlC is known as $8.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the temperature range from 25 °C to 1300 °C [20] and that of polycrystalline zirconium is reported as $7.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ below 870 °C and $9.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ at higher temperature [21]. Thus, the thermal expansion mismatch during laser surface treatment does not appear to be significant reason for the microcrack formation. Separate experiments on laser surface treatment of uncoated Zry-4 substrate at 900 °C for 3 second dwell time did not result in any phase transformation or surface damage. We therefore speculate that the microcracks may have resulted from the internal stresses accumulated due to the amorphous to crystalline transformation of the coating during the laser surface treatment. In a companion work being performed by the authors on similar laser surface treatment of PVD Zr-Al-C MAX phase coatings, no microcracks were observed. Clearly, further optimization is needed to fabricate crack free crystalline Ti_2AlC coatings. The main scope of the current study is to demonstrate the capability of laser surface annealing to induce amorphous to

crystalline phase transformation in PVD MAX phase coating without inducing phase transformation in the underlying Zr-alloy substrate.

4. Conclusions

An assessment of laser surface treatment to modify the properties of Ti-Al-C coatings (1 to 5 μm) deposited on a zirconium-alloy substrate using magnetron sputtering technique has been performed. The intended application was to improve the performance of LWR fuel cladding, the findings are readily applicable to other applications as well. The as-deposited Ti-Al-C coating was amorphous and laser surface treatment to produce a surface temperature of 900 °C for 3 seconds was sufficient to transform the amorphous phase into a Ti_2AlC crystalline phase without any significant alteration in the microstructure of the underlying Zircaloy-4 substrate. [Computational thermal analysis via commercial finite element software](#) was applied to guide the selection of parameters for laser surface treatment, particularly in regards to heating the coatings to induce a crystalline to amorphous transformation while maintaining the substrate temperature below 850 °C. Mechanical integrity of the coatings was confirmed using wear and scratch tests, with laser-treated samples outperforming as-deposited samples, and both conditions offering improvements over the behavior of bare Zircaloy-4, even though the laser-treated surface showed micro-cracking. A steam autoclave test was performed at 400 °C and 10.3 MPa for 72 hours clearly confirmed the protective nature of the as-deposited and laser-annealed coatings. The morphology and size of the oxide particulates varied markedly between the as-deposited and laser-treated coatings. Further work is needed to optimize parameters for laser surface treatment to eliminate the formation of microcracks.

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6. References

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Table Caption

Table 1: Summary of the magnetron sputtered samples of Ti-Al-C coatings deposited and investigated in this study showing their compositions, thicknesses, and tests for which they were used.

List of Figure Captions

Figure 1: (a) Schematic diagram of the various laser processing parameters used on the coating in preliminary studies, (b) photograph of the coating (sample 1) after preliminary studies with multiple laser parameters, and (c) photograph of the laser treated coating (sample 6) on the entire area with optimal parameters.

Figure 2: SEM images of surface of as-deposited coating (sample 1) at (a) low magnification and (b) high magnification. (c) X-ray diffraction (XRD) peaks of as-deposited coating (sample 1) showing predominantly peaks from the underlying zirconium substrate and an amorphous signal from the coating.

Figure 3: SEM images of the surface of laser surface annealed coating (sample 1) on regions subjected to laser treatment at (a) 3 s at 1100 °C and (b) 1 s at 700 °C.

Figure 4: XRD peaks of as-received Zry-4, as-deposited coating (sample 1), and from regions subjected to various laser treatments of surface temperature and dwell time, as indicated. Circles refer to Ti_2AlC peaks and cross marks refer to TiAl phase.

Figure 5: Numerical simulation of the laser annealing: (a) a processing image, (b) temperature evolution of the top surface and bottom surface at a fixed position ($x=12$ mm and $y=0$ mm in Figure 5a). The dark arrow indicates the motion of the laser spot.

Figure 6: (a) Surface temperature and laser power during continuous large-area laser treatment. Laser power was adjusted by feedback from surface temperature response, (b) XRD peaks of the laser-annealed coating (sample 7) showing an amorphous to crystalline transformation in the coating. The unmarked peaks are zirconium substrate peaks. (c) SEM images of laser surface treated coating (sample 7) showing the formation of microcracks in the coating, and (d) cross-

sectional view of FIB image of laser annealed coating (sample 8) indicating that some microcracks may propagate into the substrate (the red arrow indicates Ti_2AlC coating).

Figure 7: SEM plan view images of wear test and scratch test; (a) and (d) are uncoated Zry-4 substrate, (b) and (e) are the as-deposited coating (sample 4), and (c) and (f) are the laser-annealed coating (sample 8). Note in table 1 that coatings have nearly identical stoichiometries and have a thickness of 2 μm thickness.

Figure 8: SEM and EDS images of samples after testing 400 °C and 10.3 MPa for 72 hours in a steam environment autoclave test. The first row images are plan view and the second row images are cross section view; (a) and (d) are uncoated Zry-4, (b) and (e) are as-deposited coating (sample 3), and (c) and (f) are laser-annealed coating (sample 6). The red arrows indicate oxygen rich areas at the coating-substrate interface.

Figure 9: XRD peaks of uncoated Zircaloy-4 surface, as-deposited surface (sample 3), and laser-annealed surface (sample 6) after the steam autoclave corrosion tests.

Table 1

Sample ID	Coating Thickness (µm)	EDS Analysis of Coating (Average from 3 Spots)						Test
		Ti		Al		C		
		Atomic %	Std Dev	Atomic %	Std Dev	Atomic %	Std Dev	
TiAlC#1	5	46.51	0.60	33.39	0.99	20.10	0.49	Laser optimization
TiAlC#3	2	45.18	0.20	26.20	0.13	28.62	0.10	Corrosion test
TiAlC#4	2	45.79	0.29	27.14	0.37	27.06	0.14	Mechanical test
TiAlC#6	2	42.29	0.22	27.66	0.52	30.05	0.34	Laser annealing → Corrosion test
TiAlC#7	2	44.22	0.61	27.81	0.79	27.97	1.40	Laser annealing → Corrosion test
TiAlC#8	2	43.63	1.48	27.84	1.46	28.53	0.47	Laser annealing → Mechanical test

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9