Silicon carbide coatings on zirconium alloy for light water reactor fuel cladding studies

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Abstract. Coating of zirconium alloys is a promising approach for improving various properties of the cladding of fuel elements, including physical, mechanical properties, corrosion resistance and reduction of radiation damage. In this paper, SiC coatings with thicknesses of 100, 200, and 300 microns were deposited by selective laser sintering (SLS) on Zr-1Nb alloy substrates at a laser power of 150 W. The 200 µm layer deposition registered the least contact depth during macro-scratch test to a maximum depth of about 25 µm into the coating. The uniformity and less porosity of the coatings is observed on the transverse sections in the entire variant. Analysis of the phase composition of the coating revealed the formation of silicon carbide phases (6H & 4H), with protective oxides of Al2O3, Y2O3, SiO2 and YAlO3. High coating adhesion was noticed with results of the scratch tests showing no delamination regardless of the higher loads used. However, partial chippings and transverse cracks were observed. The results obtained indicate the need for further research to improve the porosity of the surface structure of the coating and to conduct other necessary tests.

1. Introduction
Since 2011 following the tragic Fukushima Daiichi Nuclear Power Plant accident, the quest for Accident Tolerant Fuel (ATF) has become extremely essential towards shaping the safety path of future nuclear industries. Though zirconium-based alloys have gained acceptance over decades in the nuclear industry, the submissiveness of zirconium during Loss of Coolant Accident (LOCA) event in which the oxidation response of zirconium at a higher temperature speedily deteriorates in its integrity under such condition calls for the need in enhancing the next generation of cladding materials [1].

Thin coatings are anticipated to have marginal importance in terms of the thermomechanical properties of zirconium-based claddings [2]. After Fukushima nuclear disaster, two major technical directions of designing an enhanced cladding systems towards the replacement of existing LWR fuel cladding components were proposed. The first direction includes: SiCf/SiC composites [3], FeCrAl [4], molybdenum alloys [5] and MAX phases as an alternative material for fuel cladding. The second direction involves the protection of the surface of currently used zirconium alloys by coatings [6], such as Cr coated Zr-alloy, SiC coated Zr-1Nb, etc. This approach in enhancing the fuel cladding tube are expected to be deployable in the short term. Also, these coatings do not exceptionally change the central physics in LWRs but are likely to improve the heat transfer performance of the cladding. Some studies have proven various depositions on zirconium-based alloy effective in overcoming oxidation, resisting corrosion and minimizing the vulnerability of grid-to-rod fretting failures [7]. Based on
published works, ATF coating material composition should have at least Cr, Al or Si in order to form any of the protective oxide phases (Cr2O3, Al2O3, and SiO2) in strengthening the underlying material. Figure 1 is a schematic breakdown of the various technical issues with time of development.

![Schematic diagram of technical issues and time to development](image)

**Figure 1.** Consideration of the technical issues and time to development of the ATF cladding [8].

Ceramic coatings involving TiN, TiAlN, Ti3SiC2, Ti2AlC and SiC have been investigated in recent times, however, SiC has more outstanding properties than most ceramics. Hence, there is the need to further investigate SiC depositions with several 3D printing techniques to compare their various properties in order to make the right choices of factoring cost, time and efficiency of the fabrication methods engaged. Therefore, this study aimed at depositing SiC composite coatings on Zr-1Nb alloy substrates using the SLS technique, followed by microstructural, phase composition, elemental composition and scratch adhesion investigations of the coated surface.

### 2. Research materials and deposition methods

A sample of dimensions (40 mm × 25 mm × 2 mm) of the E110 (Zr-1Nb) alloy substrate was polished and cleansed with acetone on all faces and measured at an average roughness of 0.3 µm with the Hommel tester T1000. The SLS system was equipped with the Ytterbium fiber laser (IPG Photonics, Moscow, Russia) of 1070 nm output wavelength and 500 W maximum power. SiC powder (grade: SIKA DENSITEC L, Norway) was used in this research. Deposition of the SiC on the substrate was performed at coating thicknesses of 100 µm, 200 µm, and 300 µm, respectively, as indicated in table 1.

### Table 1. Parameters used in the SLS fabrication

| Laser power (W) | Scanning time (µs) | Laser speed (mm/s) | Deposition thickness (µm) | Atmosphere |
|----------------|-------------------|-------------------|--------------------------|------------|
| 150            | 600               | 25                | a 100                    | Air        |
|                |                   |                   | b 200                    |            |
|                |                   |                   | c 300                    |            |

![Diagram of Zr-1Nb substrate deposition](image)
Figure 2. Schematic process involved in coating of SiC on Zr-1Nb: (i) Initial substrate dimensions, (ii) Polished and wiped with acetone filled cloth (iii) SiC deposited (iv) Actual macrograph

3. Results and discussions
Figure 3 is a micrograph showing the weakest portions of the coating variants a, b and c corresponding to 100, 200 and 300 µm thick deposition respectively using the TESCAN VEGA3 SEM system. These surfaces were characterized by fewer shallow trenches, coarse-grained structures with few micro-cracks in the 100 µm deposition. It was observed that thicker coatings present more uniformity compared to the 100 µm thick variant. Figure 4 shows a cross-section of 100 µm thick deposition. It can be observed that about 40 µm coating layers were embedded into the substrate to keep the coating firm into the zirconium substrate. Coating cross-section observed at higher magnification exhibited less porosity in the grain boundaries as shown in the figure 4c.

Figure 3. Micrograph of the surface morphologies of coated samples

Figure 4. Micrograph showing the cross-sections through coating and substrate of 100 µm deposition
Figure 5. Elemental composition of sintered SiC coating surface

The SEM/EDS TESCAN VEGA3 set-up was engaged in investigating the elemental composition of the coating surfaces. The figure 5 shows the statistical distribution of the coated surfaces. The Ai, Aii and Aiii represents three different areas on the 100 µm thick layer with their respective elemental distribution while the B and C variants represents that of the 200 µm and the 300 µm thick variants respectively. One major observation from EDS results was the higher level of oxygen present on the coating which also can be confirmed in the figure 6 showing the various phases present on the coated surfaces. The quantity of oxides in this samples can be attributed to the manufacturing of the coating in an air environment which exposes the sintering fabrication to oxygen in the chamber. This could lead to accelerated oxidation hence future coating will be focused on lessening the formation of oxides by manufacturing the coating in an inert filled chamber.

Phase composition investigation was carried out with XRD 7000 diffractometer maxima (Shimadzu, Kyoto, Japan) on SiC composite before and after the deposition. This system measurement condition includes an X-ray Cu target, voltage (40kV), current (mA), divergence slit of 1 degree and scan range from 10° to 90°. SiC composite used in this study comprises of seven main phases including SiC(6H), SiC(4H), Y2O3, Al2O3, SiO2, Si, and YAlO3 phases. The Fig. 6 shows the X-ray diffraction pattern observed on the coated surfaces after the SLS deposition.

Figure 6. Phase composition of the sintered SiC composite on substrate

Nano to micro scratch tests were incompatible to the coating due to the higher level of adhesiveness exhibited by the coatings, hence macro-scratch test was carried out involving constant loads of 50 N to 100 N. The adhesion scratch test on the coating were carried out with the Rockwell cone, apex angle 120 with diameter 200 microns. Figure 7 shows the scratch paths and its associated
features. SEM observations along the coating paths reveal less degradation despite the higher magnitude of load exerted by the diamond stylus during the test. No major spallation was observed but chippings along both sides of the grooves. Conformal cracks on a microscale forms while coating conforms to the groove as exhibited on figure 6e. EDS elemental compositions taken along the scratch path from figure 6e shows the presence of some remains of the coating material composition such as Si (18.65), O (37.18%), Al (3.06%), and substrate material Zr (41.12%).

**Figure 7.** Scratch paths created by stylus with constant loads of 50 N and 100 N on (a) 100 µm, (b) 200 µm, and (c) 300 µm specimen (d, e) a typical scratch path and its associated features

**Figure 8.** Scratch profile and corresponding length along the scratch path (a, b, & c represents profiles for a constant load of 50 N and d, e, & f for 100 N load for 100, 200 and 300 µm layer respectively
The figure 8 shows the frictional scratch profile depth along the scratch path of 5 mm long. Constant loads of 50 N and 100 N produce slightly similar patterns on the same sample. The 200 µm layer sample (figure 8 b & e) registered the least contact depth followed by the 100 µm coating layer (figure 8 a & d) whiles the highest depth was registered in the 300 µm thick deposition sample (figure 8 c & f). As can be observed clearly from the figure 8, most of the scratch profiles depicted an increase in the scratch contact depth as the indenter moves along the scratch track except for those of the 200 µm thick layer deposition where the depth increases from the start of the test and falls as approaching the end of the 5 mm length. Scratch width remains approximately the same from the start to the end of the scratch track while tracks created with the 100 N load slightly widens in width as compared to the tracks created by 50 N load.

4. Conclusion
SiC micro-composites were deposited on Zr-Inb alloy substrates at 100, 200, and 300 µm for cladding material studies. Experimental investigations and analysis involving SEM surface structure, XRD phase composition, EDS elemental composition and scratch adhesion of the coating were carried out to understand the major changes in the coating microstructure. SEM surface structures reveal coarse grained, shallow trenches in all variants while better uniformity was achieved in the higher layer thick variants. Uniformity and less porosity are established in the cross-sections as observed at higher magnification. Phase compositions including β-SiC (6H), SiC (4H), Si and essential oxides for strengthening the coating on the underlying substrate such as Al2O3, Y2O3, SiO2 and YAlO3 were recorded on the coating surface to sub-surface. Macro scratch test results show fewer deteriorating effects with the 200 µm variant registering the least contact depth. Non-uniformity of the frictional force profile can be attributed to the various grain boundaries of the sintered particles encountered by the indenter as it crosses from boundary to boundaries. Finally, obtained results provides the foundation for further research towards surface modified zirconium alloy for fuel cladding studies.

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