Preliminary Study of Zirconium Carbide Ceramic Deposition on Austenitic Stainless Steel by Pulsed Laser Deposition

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Abstract. Coating Zirconium Carbide (ZrC) on the stainless steel (SS) will increase the corrosion resistance of SS which suffer from the intergranular attacks during operation as construction materials in reactors. ZrC coating have been partially deposited on Austenitic 316L SS by Pulsed Laser Deposition (PLD) at 800°C temperature substrate with constant oxygen flow injection of 40 sccm (Standard Cubic Centimeters per Minute), chamber pressure around 229-244 mTorr and 105 the numbers of laser shots. The sample was analyzed using X-Ray Diffraction (XRD), Microscope Optic (MO), Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscope (SEM-EDS), and Atomic Force Microscope (AFM) to characterize the phase, morphology, thickness of the films and surface topography. The results showed that the thickness of the thin film around 4.93-8.10 µm with 49.6 nm surface roughness. The film surface was very smooth. The present of Zr and C was detected in SEM & EDS results but not appeared in XRD pattern, possibly due to diminish tension of the thin films on the substrates caused by low lattice mismatch between ZrC and Austenitic 316L SS substrate. Furthermore, ZrO₂ phase has been found on the substrate which is predicted because of the interaction between ZrC target and oxygen background gas.

Keywords: Zirconium Carbide, Stainless Steel, Coating, Pulsed Laser Deposition

1. Introduction
Austenitic stainless steels are materials that very important in both conventional and advanced reactor technologies, especially in their application as cladding material. Austenitic stainless steels 316L used reactors construction materials in worldwide [1]. Beside that, because of its good corrosion resistance and good compatibility with hot sodium, 316L SS used in the core of sodium cooled fast reactors [2].

During operation in stainless steel, several problems was found. Stainless steel suffers from intergranular attacks which result in the loss a plasticity and strength because of crystal structure deformation caused by a localized attack along the grain [3]. Beside that, irradiation can modify the dislocation contributions, which can harden the SS. These problems may impact the life extension in the reactor [3].

Coating method is one of the methods that will increase the corrosion resistance of SS. By employing the coating can be protect the SS substrate against several problem above in high temperatures. Coating based Al₂O₃ and NiAl cement showed the excellent performance to protect on the high temperature corrosion. However, they are very bad as thermal insulator than ceramics [4].
Ceramic ZrC is being considered for increase the corrosion resistance of SS. ZrC has high melting point (3532°C), high hardness number (25GPa), good wear resistance and high thermochemical stability [5]. Xin et al stated that ZrC have attached much attention due to low cost, their relatively low density, excellent ablation resistance and good strength at high temperatures [6].

Several deposition techniques have been applied to obtain the thin film such as Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD). ZrC coating have been done by CVD, but the result showed that CVD consume much time due to the low deposition rate, thus increasing the manufacturing process and limited application [6]. Some report said the deposition was not being deposited well. Sunil A used radio frequency cold plasma assisted chemical vapor deposition (CVD) to coated ZrC on a mild steel substrate [7]. But the result showed that ZrC layer was not deposited on the substrates which caused by inadequate vacuum and or the leak of oxygen to the reactor [7]. Another deposition technique, PVD have been employed to obtain ZrC thin film for various application [4,7-9]. One of the PVD techniques is PLD which a very sustainable technique for produce the protective coating. Craciun et al deposited the ZrC thin films on (100) Si substrate of 500°C by PLD and have confirmed the elemental composition of the deposited films by AES and XPS. Several problems of non-uniform thickness of coating and wettability have been found on the ZrC films [5].

In this study, ZrC ceramic was used as coating materials on austenitic stainless steel (316L) using PLD and the purpose is to develop the thin film ZrC with smooth roughness of surface and uniform thickness coating.

2. Experimental method

2.1. Materials
316L SS was used as substrate with chemical composition (in wt%) of steel as following: 17.2 Chromium, 10.9 Nickel, 2.1 Molybdenum, 1.6 Manganese, 0.02 Carbon and balance Iron. The surface of substrates was prepared by grinding, polishing to maintain the clean surface, and sandblasted with 0.05 microns alumina particle. Sandblasted with alumina particle can enhancing the adhesion strength between substrate and coating [3]. For coating, round shape of ZrC target was used with 6,73 g/cc density and 99.9% purity by Beijing Loyal Target company.

2.2. Sample preparation
Thin films of ZrC have been deposited on austenitic steel 316L SS using Pulsed Laser Deposition (PLD) at laboratory facilities of Center For Science and Technology of Advanced Materials – National Nuclear Agency of Indonesia. This PLD use Nd:YAG solid state laser with the 266 nm wavelength and ~ 100 mJ energy. The ZrC thin film was deposited in 800°C temperature substrate with the constant oxygen flow injection of 40 sccm (Standard Cubic Centimeters per Minute) that produce a chamber pressure around 229-244 mTorr and the numbers of laser shots were 10^3.

After deposition, the samples were analyzed using X-Ray Diffraction (XRD), Microscope Optic (MO), Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscope (SEM-EDS), and Atomic Force Microscope to characterize the phase, morphology, thickness of the films and surface topography.

3. Results and discussion
The thickness of the samples was analyzed from the cross section of the samples with MO and SEM. Figures 1 show that thickness of the ZrC thin film deposited in 316L SS was 4.93-8.10 µm.
Figure 1. Cross Section of ZrC film deposited in 316L SS (a) Optic result and (b) SEM result.

Figure 2. AFM topography analysis of ZrC deposited in 316L SS. The results show that the roughness layer of ZrC deposited in both of 316L SS have a nano-meter scale. The Ra value of sample has 49.6 nm. The roughness value of the sample is smaller if we compare to the Craciun’s et al works [4], which the roughness value around 4-6 micrometer. The films surface was very smooth. It’s found that deposition using PLD could minimize the formation of micro porous and could develop very smooth layer [10].

Figure 3. SEM result of cross section ZrC film deposited in 316L SS.

Table 1. EDS result with the position indicated in Figure 3

|   | Cr (wt%) | Ni (wt%) | Mo (wt%) | Zr (wt%) | Fe (wt%) |
|---|----------|----------|----------|----------|----------|
| 1 | 15.77    | 10.93    | -        | 1.92     | Balance  |
| 2 | 15.11    | 9        | 1.69     | -        | Balance  |
EDS result showed element on the position 1 point area as thin film and position 2 square area as substrate. The result showed that the substrate element composition was Chromium iron nickel with composition above confirmed as austenitic stainless steel. Position 1 showed the Zr element. However, the wt% of Zr is relatively small, it can be obtained that the number of Zr deposited on substrate was very small.

![Figure 4. XRD Pattern of ZrC film deposited in 316L SS.](image)

The phase of the samples was investigated by XRD (PANalytical) using Cu Kα radiation (λ= 1.5406 Å). Figure 4 shows the XRD pattern of ZrC film deposited in 316L SS. The XRD pattern showed that ZrC peaks was not observed in the 316L SS deposited. This result contributed to the small number of ZrC deposited on the substrate as shown in EDS result. So, ZrC partially deposited in the 316L SS. This happen because of the diminish tension of the ZrC thin films on the substrate. The lattice parameter of ZrC is 9.386 Å (#00-032-1489) while the lattice parameter of Austenitic SS is 3.5911 Å (#00-033-0397). This low lattice mismatch contributed to the low-quality epitaxial growth so ZrC can’t be fully deposited to the austenitic SS.

The XRD pattern of 316L SS deposited showed small peak of ZrO₂ at 2θ=30.19 which identified as main peak of ZrO₂ tetragonal (#00-080-0784). The formation of small ZrO₂ phase was possible because Zr ions due to plasma ablation from ZrC target interacted with O²⁻ from the environment. The formation of ZrO₂ phase can be made because the film was deposited in oxygen flow injection. This result confirmed with Sunit et al works, they deposited ZrC on Zr-alloy substrate using the CVD technique [6]. Zr and C presented in EDS result but not presented in XRD pattern, means the ZrC layer partially deposited on the substrate. This attributed to inadequate vacuum and or the leak of oxygen [6].

4. Conclusion
The thin layer of ZrC have been partially deposited in austenitic 316L SS using PLD with temperature substrate was 800º C. The thickness of the thin film around 4.93-8.10 µm with 49.6 nm surface roughness. The films surface was very smooth. The present of Zr and C was detected in SEM & EDS results but not appeared in XRD pattern, possibly due to diminish tension of the thin films on the substrates. It can be established that ZrC was partially coated on the surface of the substrate. Small portion of ZrO₂ have been found on the substrate because the film was deposited in oxygen flow injection. Therefore, to improve the quality of thin film the background gas should be replaced with non-oxygen containing gas.

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