Investigation of Zirconium Carbide Ceramic Coating on Surrogate Kernels Deposited by Plasma-Pulsed Laser Deposition: A Preliminary Study

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Abstract. High Temperature Gas-cooled Reactor (HTGR) is one of advanced nuclear reactors with high safety system feature. Indonesia has a plan to build HTGR as an Experimental Power Reactor (in Indonesian: RDE - Reaktor Daya Eksperimental). One of the safety system feature is its fuel system. There are two types of fuel of HTGR i.e. pebble bed type and prismatic type which all of the types are containing TRISO (Tri-Structural Isotropic) which consist of Inner Pyrolytic Carbon, SiC (Silicon Carbide) dan Outer Pyrolytic Carbon. One of the issues of the system is silver (Ag) and palladium (Pd) as the fission product could interact with SiC layer and cause corrosion. One of the candidate to resolve the issue is to replace SiC with ZrC (Zirconium Carbide). In this preliminary study, Zirconium Carbide ceramic has been deposited on a surrogate (uranium-free) fuel microkernels using PLD Plasma-Pulsed Laser Deposition. The parameter during ZrC deposition were temperature of 850°C for the substrate, the number of laser shots of 90,000 and the oxygen background gas with 40 sccm (standard cubic centimeters per minute) with the chamber pressure of 235 mTorr. Thereafter, the samples were analyzed using OM - Microscope Optic, SEM-EDS - Scanning Electron Microscope – Energy Dispersive X-ray Spectroscope, XRD – X-Ray Diffractometer and AFM – Atomic Force Microscope. The results exhibited that the ceramic coating could deposited on the surface of the substrate surface with homogeneously and sticky. The surface was very smooth within the nano-meter range order of ~80-120 nm of surface roughness. Nevertheless, the results indicated that some of ZrC was react with oxygen at high temperature on the surface of the sample and deposited on the surface of surrogate microkernels.

Keywords: HTGR, ZrC, Ceramic, PLD, Surrogate

1. Introduction
In Indonesia, 10 MW HTGR High Temperature Gas-cooled Reactor - experimental power reactor (RDE – Reaktor Daya Eksperimental) is on-going progress which was firstly introduced to BAPPENAS - Badan Perencanaan Pembangunan Nasional (National Development Planning Agency) at the beginning of 2014 and it is expected to be operable in years 2022/2023 [1]. HTGR is one of promising advanced nuclear reactors because of its high safety system feature. One of the safety system feature is its fuel system. In general, there are two types of fuel of HTGR i.e. pebble bed type and prismatic type which all of the types are containing TRISO (Tri-Structural Isotropic) which consist of Inner Pyrolytic Carbon, SiC (Silicon Carbide) and Outer Pyrolytic Carbon. One of the issues of the system is silver (Ag) and palladium (Pd) as the fission product could interact with SiC layer and cause corrosion [2-8]. One of the candidate to resolve the issue is to replace SiC with ZrC (Zirconium Carbide) [2-8]. ZrC is attractive for nuclear fuel material because of its superiority properties i.e. refractory and chemically stable compound, high melting point of 3540°C, favorable thermal and...
mechanical properties, high thermal conductivity at very high temperatures, and low neutron absorption cross-sections.

Up to now, the deposition of ZrC is mainly using CVD (chemical vapor deposition) technique. Nevertheless, one of the issues are the roughness and microporous of coating formation. One of the techniques to overcome the issue is using PLD - Pulsed Laser Deposition which could form very flat and smooth surface in the range order of nano-meter. Therefore, in this preliminary study deposition of zirconium carbide ceramic using PLD technique has been studied. ZrC was deposited on a surrogate (uranium-free) fuel microkernels as a simulation of uranium- microkernels at Center For Science and Technology of Advanced Materials (PSTBM - Pusat Sains dan Teknologi Bahan Maju) laboratory of National Nuclear Energy Agency of Indonesia (BATAN – Badan Tenaga Nuklir Nasional). The aim of this study is to investigate the characteristics of PLD technique for deposition of ZrC on microkernels and its potentials for development of HTGR’s fuel.

2. Experiment

PLD - Pulsed Laser Deposition was used for ZrC (Zirconium Carbide) ceramic deposition on surrogate (non-uranium) micro-kernels. As for comparison, ZrC has also been deposited on stainless steel substrate of SS410 at the same time and parameter. Figures 1 show the schematic of the PLD and the formation of plume during deposition. Through a glass window of PLD’s chamber the appearance of the plume is able to be seen and analyzed during deposition. Table 1 shows the experiment parameter condition with ZrC (Zirconium Carbide 99.5%) as the target for the deposition. This PLD use solid state laser of Nd:YAG with the wavelength of 266 nm with ~100 mJ of energy. The constant oxygen flow of 40 sccm (Standard Cubic Centimeters per Minute) was injected that produce a relatively-constant chamber pressure of 235 mTorr during the deposition process. The numbers of laser shots was $9 \times 10^4$ with 850°C of the substrate temperature during deposition.

![Figure 1. PLD – Pulsed Laser Deposition (a) Device system (b) Schematic (c) samples preparation.](image)
Table 1. Parameter of experiment

| Parameter                | Condition                                |
|--------------------------|------------------------------------------|
| Target material          | ZrC (Zirconium Carbide) 99.5%             |
| Substrate material       | Surrogate (non-uranium) micro-kernels     |
| Substrate Temperature    | 850 °C                                   |
| Amount of shots          | 90,000                                   |
| Chamber pressure         | ~235 mTorr                               |
| Gas background           | Oxygen                                   |
| Laser wavelength         | 266 nm                                   |
| Laser energy             | ~100 mJ                                  |
| Laser frequency          | 10 Hz                                    |
| Laser repetition pulsed  | 5 ns                                     |

Thereafter, SEM-EDS Scanning Electron Microscope coupled with Energy Dispersive X-ray Spectroscope, OM Optical Microscope, XRD X-Ray Diffractometer and AFM Atomic Force Microscope were employed to analyze the characteristic of the samples.

3. Results and Discussion

In order to analyze the microstructure of the ceramic coating layer on surrogate (uranium-free) fuel microkernels samples the OM optical microscope and SEM-EDS were employed. Figures 2 show Optical Microscope (a) and SEM micrographs of sample’s surface of surrogate (uranium-free) fuel microkernels without deposition and with deposition of ZrC.

![Figure 2](image_url)

Figure 2. Optical Microscope (a-b) and SEM micrographs (c-d) of surrogate (uranium-free) fuel microkernels samples’s surface to investigate the ZrC layer deposition with 90,000 laser number of shots (a) without deposition (b) with deposition (c) without deposition (d) with deposition
The results of Optical Microscope showed that the diameter of surrogate (uranium-free) fuel microkernels samples without ZrC deposition is ~508 μm. Then, the diameter of surrogate (uranium-free) fuel microkernels samples with ZrC deposition is ~518 μm. It was found that the diameter of surrogate (uranium-free) fuel microkernels sample increased ~10 μm after deposition. It could be analyzed that the target of deposition was deposited on the samples with the thickness of ~5 μm. The SEM characterization showed the microstructure morphology of the surface of the surrogate (uranium-free) fuel microkernels samples without and with deposition. The surface after deposition was rougher than without deposition. It showed that the target could deposited on the surface of surrogate (uranium-free) fuel microkernels samples. Furthermore, it was found that thin film as the coating layer could deposited on the surface of surrogate (uranium-free) fuel microkernels samples with homogeneously and sticky. There was no porous found on the surface of the coating layer.

The EDS analysis of the surrogate (uranium-free) fuel microkernels samples was used in order to analysis the chemical composition of the coating layer after deposition as shown in Figures 3. The purpose is to investigate chemical analysis of the coating layer i.e. zirconium, carbon and oxygen elements. Therefore, the analysis of zirconium, carbon and oxygen percentages on the surrogate (uranium-free) fuel microkernels samples with various positions was analyzed as shown in Table 2.
Figure 3. SEM micrographes of surrogate (uranium-free) fuel microkernels samples’s surface (a) specific area analyses of coating layer on the surrogate (uranium-free) fuel microkernels samples with various positions (b) area 001 (c) area 002 (d) area 003

Table 2. Analyses of EDS for zirconium, carbon and oxygen element percentages of coating layer on surrogate (uranium-free) fuel microkernels samples’s surface with various positions

| Elements / Parameter | Area 001 | | | Area 002 | | | Area 003 | | |
|---------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|                     | % mass  | % atom  | % mass  | % atom  | % mass  | % atom  | % mass  | % atom  |
| Zr                  | 75.36   | 29.98   | 71.63   | 26.31   | 70.18   | 24.85   |
| C                   | 18.76   | 56.67   | 20.55   | 57.32   | 22.28   | 59.92   |
| O                   | 5.89    | 13.35   | 7.82    | 16.37   | 7.54    | 15.23   |

The results of SEM-EDS characterization showed that the surface of surrogate (uranium-free) fuel microkernels samples was consist of zirconium, carbon and oxygen element. Furthermore, the zirconium, carbon and oxygen percentage was found in various positions with similar composition ratio. The results showed that zirconium carbide and zirconium oxide were formed on the surface of surrogate (uranium-free) fuel microkernels samples. Zirconium oxide was formed because during deposition at high temperature of 850°C some of zirconium was react with oxygen as the background gas on the surface of surrogate (uranium-free) fuel microkernels samples. Nevertheless, it was found that the coating layer was homogeneously deposited on the surface area of surrogate (uranium-free) fuel microkernels samples indicated from distribution of zirconium and carbon element percentages.

In order to investigate the formation of the coating layer XRD was employed. For that purpose, because surrogate (uranium-free) fuel microkernels samples is too tiny, the comparison sample of stainless steel SS410 which deposited with the same time and parameter was used. Figure 4 shows the XRD analysis of the coating layer. The results indicated that zirconium dioxide (ZrO₂) was formed on the surface of the substrate. This results confirm the previous analysis using EDS. It means that during deposition some or most of zirconium element from zirconium carbide was interact and react with oxygen on the surface of substrates at high temperature and formed zirconium dioxide ceramic material. The behavior of zirconium dioxide formation from zirconium carbide at high temperature were also reported by other researchers [9-12].
Figure 4. XRD analysis of coating-layer deposition on the substrate

In order to investigate the roughness of the coating layer on the surface of substrate AFM-Atomic Force Microscope was employed. For that purpose, because surrogate (uranium-free) fuel microkernels samples is too tiny, the comparison sample of stainless steel SS410 which deposited with the same time and parameter was used. Figures 5 show the AFM topography analyses of the coating layer’s surface with 2 and 3 dimensions.
Figure 5. AFM analyses on the surface of coating layer surface (2 dimensions with line scan roughness analysis and 3 dimensions) (a) 2 dimensions (b) 3 dimensions

The results exhibited that the coating layer’s surface roughness of on the substrate was in ~80-120 nm. It means that the PLD technique could grow and produce very smooth coating layer within nano-meter scale of surface roughness that potentially minimize the formation of porous in micro and nano-meter scale.

4. Conclusions

Target of ZrC (Zirconium Carbide) ceramic has been successfully deposited on surrogate (uranium-free) fuel microkernels samples using the technique of PLD - Pulsed Laser Deposition with the substrate temperature of 850°C and 235 mTorr of chamber pressure that was controlled from injection of constant oxygen flow of 40 sccm, and with the amount of laser shots $9 \times 10^4$. The results exhibited that the ceramic coating could deposited on the surface of surrogate (uranium-free) fuel microkernels samples and a comparative substrate with homogeneously and sticky. The surface roughness of coating layer was very smooth in the nano-meter scale range order. The results indicated that some of the zirconium carbide deposition was react with oxygen at high temperature on the surface of the sample and deposited on the surface of surrogate microkernels. In order to gain high purity of zirconium carbide deposition on the surface of microkernels, the inert background gas should be used even though the target is ceramic materials. Nevertheless, the general results exhibited that the technique of PLD has potential to be applied for coating of ZrC for the development of high performance microkernels of HTGR’s fuel.

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